VOL. VIII. [JUNE, 1886.] No. 3.

AMERICAN

CHEMICAL JOURNAL.

ON THE CHANGES EFFECTED BY HEAT IN THE CONSTITUTION OF ETHYLENE.[1]

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Many of the simpler phenomena of destructive distillation have been observed during the study of such substances as marsh gas and ethylene. The comparatively simple constitution of these compounds has led to the belief that their decomposition by heat would yield well-defined reactions, from which valuable generalisations might be drawn. Definite statements are accordingly made in many text-books concerning the action of heat upon ethylene; but comparison of them shows much that is inconsistent, arising, doubtless, from the fact that this point has entered as a secondary feature in many investigations on other themes, leaving the literature in a somewhat confused state. In attempting to use the effect of heat upon ethylene as the starting-point of another investigation, it became necessary to collect the scattered literature and to supplement it by the following work, in which some new facts have been developed.

When the Dutch chemists Deimann, Van Troostwyk, Lauwerenburg and Bondt[2] first recognised the difference between ethylene

[1] From the Author's Thesis for the Degree of Doctor of Philosophy in the Johns Hopkins University.

[2] Annales de Chimie et de Physique, 1st series, **21**, 48; Nicholson's Journal **1**, 44; Gilbert's Annalen **2**, 201.

and marsh gas, they tried to fix the conditions under which ethylene is formed by heating the vapor of alcohol, and for this purpose examined the action of heat upon ethylene. They stated that, 1. ethylene when heated did not decrease in volume; 2. it lost the property of forming an oily liquid with chlorine; 3. the tube in which it was heated was blackened and covered by drops of empyreumatic oil. At the request of the Philomathean Society of Paris, Fourcroy, Hecht and Vauquelin[1] repeated some of these experiments, and showed that at high temperatures ethylene yields a considerable proportion of hydrogen, carbon is deposited, and no ethylene remains unchanged.

The formation of ethylene during the dry distillation of many organic bodies was noticed by William Henry[2] in 1805, who also noted the fact that ethylene can yield the other common products of dry distillation when further heated. He showed,[3] also, that by passing electric sparks through ethylene for a sufficient time the volume increased, and on exploding the gas with oxygen less carbon dioxide was obtained than before the sparks had been passed. By calculating from the deficit of carbon dioxide the amount of ethylene which had disappeared, it was shown that the increase in volume was equal to twice the volume of ethylene which disappeared. The reaction was not complete, but it showed that all the ethylene which entered into the reaction decomposed smoothly into carbon and hydrogen; thus:

$$C_2H_4 = C_2 + 2H_2.$$

This view was supported by the deposition of carbon in the tube. No secondary products were formed, for if they had been, they would have caused some contraction, and the carbon in them would have appeared as carbon dioxide in the subsequent analysis, so that the expansion would not have been twice the loss in carbon. These experiments were practically duplicated some years afterwards by Quet,[4] who passed sparks from an induction coil through ethylene. Carbon was deposited in the line of the sparks, so that eventually a bridge of carbon was formed between the electrodes.

The most complete investigation of the decomposition of ethylene at the temperature of the electric arc was made by H. Buff and

[1] Gilbert's Annalen **2**, 210. [2] Nicholson's Journal **10**, 65.
[3] Philosophical Transactions 1809, 446.
[4] Comptes Rendus de l'Academie des Sciences de Paris **42**, 903.

A. W. Hofmann[1] in 1860. By subjecting ethylene to red heat by means of a platinum wire traversed by a powerful current, they obtained a deposition of carbon, but no increase in volume—*i. e.*, marsh gas was formed according to the following reaction:

$$C_2H_4 = CH_4 + C.$$

The marsh gas thus formed remained unchanged at a red heat, but with the electric arc the decomposition went farther, as indicated by a permanent expansion of the gas. With electric sparks the effect was similar: the volume increased rapidly at first, then slowly. In twenty-five minutes the expansion ceased, after 7 cubic centimetres of dry ethylene had become 12.25 cubic centimetres. A bridge of carbon formed between the poles. The residual gas was hydrogen, which had an unpleasant odor and burned with a slightly luminous flame. They were careful to observe that no marsh gas was formed at this temperature.

The experiments mentioned thus far deal principally with the action of electric sparks upon ethylene. They seem to justify the following general conclusions in regard to the action of heat at the highest temperatures which it is convenient to use. The results of Henry's experiments, and, to some extent, those of the Dutch chemists, are in accordance with the conclusion expressed by Fourcroy, Hecht and Vauquelin, that the higher the temperature the greater the tendency for ethylene to yield carbon and hydrogen. The final result of heating by electric sparks is a separation of the gas into its constituents. The question arises whether this is effected by a simple separation of carbon and hydrogen, or whether the decomposition takes place in different stages, such as the formation of marsh gas and carbon, and by successive decompositions results finally in simple carbon and hydrogen. The experiments of Buff and Hofmann, as far as we can interpret them, seem to justify the conclusion that, at the highest temperatures, there is simple separation of carbon and hydrogen; for, although working with this point in view, they failed to obtain secondary products when the highest temperatures were used. No secondary products have been observed by any one, when passing electric sparks through ethylene, except De Wilde,[2] who found small quantities of acetylene; but Berthelot has obtained traces of acetylene from carbon and hydrogen alone under these conditions. The experiments of Henry

[1] Liebig's Annalen der Chemie **113**, 129. [2] Zeitschrift für Chemie, 1866, 735.

support the above conclusion, for although the decomposition was by no means complete, the only products obtained were carbon and hydrogen, together with undecomposed ethylene.

At temperatures lower than that of the electric arc the decomposition of ethylene is not so simple. This is indicated by the experiments of the Dutch chemists, of Grove, and of Buff and Hofmann to which reference has been made. The latter chemists obtained marsh gas and carbon by use of a heated platinum wire. The experiments of Grove[1] are not in strict accordance with this, but as the spirals were not necessarily heated to the same temperature, perfect agreement could not be expected. The experiments indicate, however, that the next stage preceding complete separation is a decomposition into marsh gas, without the formation of any more complex products.

Passing to still lower temperatures it is difficult to reconcile the statements of different observers as to the products formed, partly because the temperatures were not carefully observed, and distinctions are only made as to the conduct of ethylene at such temperatures as "red heat" and "white heat," while observations at still lower temperatures are altogether wanting. Usually a glass or porcelain tube is heated at temperatures varying from a "low red heat" to white heat; ethylene is passed through this tube and is examined as it issues from the other end. In this way Marchand, Magnus and Berthelot accumulated data for the principal statements made in modern text-books.

Marchand[2] passed ethylene through glass and earthenware tubes filled with fragments of earthenware heated strongly. He analysed the resulting gas by passing it over heated copper oxide and determining the carbonic acid and water as in an ordinary combustion. He stated that when the tube is heated to redness marsh gas and carbon result; at a white heat only carbon and hydrogen. His data for these conclusions are furnished by the proportion of carbon to hydrogen in gas heated to redness and collected at the other end of the heated tube at intervals of thirty to fifty minutes. At first the proportion of carbon to hydrogen was 100 carbon to 17.236 hydrogen. This represents nearly pure ethylene (100 : 16.67); the last collected corresponds (100 : 27.251) to a mixture of marsh gas and ethylene, or at least to marsh gas and some

[1] Philosophical Magazine, 3d series, **31**, 20, 91, 96.
[2] Journal für praktische Chemie **26**, 478.

compound richer in carbon than marsh gas. There is no proof that marsh gas was actually formed, except that on heating higher nearly the proportion of marsh gas was reached—*i. e.*, 100 carbon to 30.771 hydrogen. After heating at a strong white heat the carbon nearly disappeared—that is, for 100 parts carbon 6121.2 parts hydrogen were found. These results were confirmed and extended by Magnus,[1] who, in 1847, carefully investigated these phenomena. His main point was that, besides the gaseous products obtained by previous observers, liquids which he speaks of generically as "tar" are also formed when ethylene is passed through a glass tube heated to redness. Except the meagre statement of the Dutch chemists, this is the first observation of the formation of more complex products from ethylene by heat. Magnus states that ethylene (which he prepared by Mitscherlich's method and purified by passing through sulphuric acid and then through caustic potassa) heated to "incandescence" for some time in a glass tube yields tar, but when the upper part of a bent glass tube or bell jar was filled with pure ethylene and heated in a bath of easily fusible metal, "the temperature was little higher than that of boiling mercury," the gas did not have the odor of tar, but retained its original characteristic odor. "The formation of tar from olefiant gas begins, therefore, at a temperature which is at any rate higher than 360°, and it appears not to take place below red heat. At a dark red heat, however, the tar is formed in such an amount that it collects in drops." As to the nature of these liquid products little is said, except that they are only partially volatile, carbon always remaining behind. They are not always of the same character, being darker or lighter in color according to the temperature of formation. When the liquids are formed the volume of the gas is diminished. The residual gas consisted for the greater part of marsh gas, but contained also undecomposed ethylene, the vapors of tar and hydrogen. The proportions varied in different experiments. It was shown by Berthelot[2] that the liquid product obtained by heating ethylene is not a single substance, but a mixture of several liquids; among them benzene, styrene and other liquids with higher boiling-points. He found a trace of acetylene in the gaseous residue, and claimed that a large proportion of ethane was formed, and on this basis supposed that the decomposition of ethylene by heat consists in a

[1] Poggendorff's Annalen der Physik **90**, 1.
[2] Annales de Chimie et de Physique, 4th series, **16**, 144.

splitting of two molecules of ethylene into acetylene and ethane, and that the formation of liquid products is due to a subsequent condensation of the acetylene to more complex products. But there is no experimental ground for believing that this sequence is followed in the decomposition, and a careful study of the condition in which Berthelot leaves the matter does not make it clear that he has added materially to the knowledge of the action of heat upon ethylene by these reactions, as it will be observed that starting with almost any hydrocarbon a mixture of compounds can be obtained so complicated as to admit of many explanations. Berthelot's results are also different from those of previous observers, in that he finds ethane as an important decomposition product at red heat where others found marsh gas. The impression conveyed by his work that ethylene is a comparatively stable substance at 600°–700° is not in accordance with other observers.

Summing up the literature of the subject, it seems that at the highest temperatures ethylene separates directly into its elements. Below this point marsh gas and carbon are obtained, then marsh gas and several liquid products, among them benzene, styrene, etc., under certain conditions. It has also been stated by v. Wilde[1] that under the influence of a silent electrical discharge liquid products are formed in a manner somewhat analogous to the reaction by heat. It has been the endeavor of the present work to extend this knowledge in the direction of lower temperatures.

The fact that a difference is noticed in the action of heat at various temperatures leads to the questions, What is the lowest point at which heat affects the constitution of ethylene? and, What is the nature of the change at that temperature? In order to answer either of these questions, or others which easily present themselves, two conditions must be filled: 1. the gas must be heated at fixed temperatures; 2. the temperatures must be kept constant within the limits in which change is noticed until all change ceases.

In order to fill the last condition a tube of Bohemian glass thirty inches long was cleaned and dried as if for a combustion; both ends were drawn out for eight inches, the small ends were bent at a right angle and each connected by a rubber stopper with a glass cylinder, which could be filled with mercury through a tubulus near the bottom. A small glass tube passing through a second hole in the rubber stoppers served as an exit or entrance tube for

[1] Berichte der deutschen chemischen Gesellschaft 7, 357.

air or ethylene. After filling both cylinders with mercury the air in the combustion tube was displaced by ethylene and one cylinder also filled with this gas. The small conducting tubes were then closed. The ethylene could now be passed from one cylinder through the heating tube into the other cylinder by drawing off mercury from one and filling the other. Reversing this process the gas could be forced back through the heated space into the first receiver. Thus the same gas could be subjected to the heat repeatedly until no further change was noticed. By means of this apparatus the general phenomena of the action of heat upon ethylene were studied, at first with little regard to controlling the temperature exactly.

The ethylene used in all the experiments was prepared by Wöhler's method of heating alcohol and sulphuric acid in the proportion of four parts by weight of sulphuric acid to one part of alcohol, sand being added to prevent foaming. The method gave satisfactory results when only the first half of the gas was used which a given amount of alcohol was capable of yielding. Purification through a Wolff's flask containing strong sulphuric acid and two bottles of caustic soda solution proved insufficient, for the gas still contained sulphur dioxide and moisture. It was therefore purified by passage through concentrated sulphuric acid, caustic soda (four flasks), concentrated sulphuric acid (three flasks), solid caustic potassa, solid calcium chloride, and finally through a tube containing phosphorus pentoxide. This method of purification was used in all the experiments to be described; no sulphur dioxide was found in ethylene thus purified, though tests were made for it repeatedly. It was necessary to pass ethylene through the apparatus for some time before all the air was driven out.

First Series of Experiments.

Ethylene was heated for several hours in the apparatus described, at first without any attempt to determine the temperature, except by noticing that the glass softened slightly. By this means a general idea of the decomposition was obtained. It took place readily. There was blackening in the hottest part of the tube, while in the cooler parts drops of a yellow liquid condensed, and crystalline flakes resembling naphthalene were noticed. On opening the tube an odor similar to naphthalene was very evident. In a second experiment it was noticed that the drops of liquid were

at first colorless, but gave a gradation in color through yellow and brown to black in the hottest part of the tube, after the heating had been continued some time. On cooling it was found that the gas had decreased in volume. The residual gas was not analysed, for diffusion had taken place through the rubber stoppers. 5 per cent. of the gas could still be absorbed by sulphuric acid.

It was supposed that all the experiments would be made at temperatures above that of boiling mercury, and a Siemens pyrometer, depending upon the increased resistance of a platinum wire when heated, was used for determining temperature. The pyrometer consisted of a fine platinum wire placed in the tube to be heated; this was welded to thick platinum wires leading to the cool portion of the tube and dipping into the mercury in the reservoirs. The mercury was made part of an electric circuit including a resistance-box and Wheatstone's bridge. The resistance of the whole system was determined for a definite temperature, and the resistance at 0° C. calculated by Siemens' formula,

$$R_t = R_o(0.00216407\,T + 0.039369\sqrt{T} - 0.24127),$$

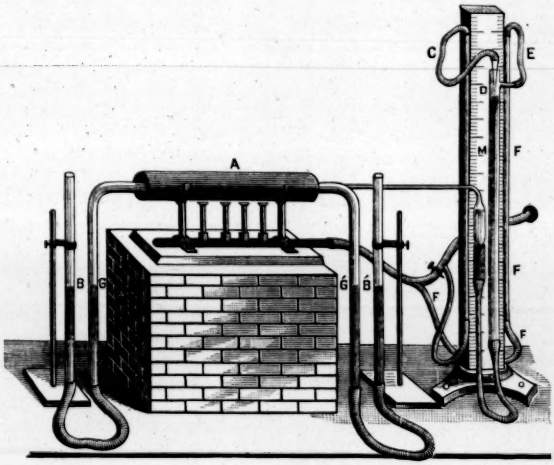
where R_o = the resistance at 0° C., R_t = the resistance at the temperature of the observation, t, and $T = t + 273°$ C. By this means it was determined that the phenomena described above can be observed at a temperature 440° C., from the following data:

$R_b = 1.282$ Siemens' units.
$R_t = 1.956$ " "

The gas used in these experiments was analysed by Hempel's absorption methods, and found to contain 96.6 per cent. ethylene as the mean of four determinations. The remaining 3.4 consisted of air.

In order next to determine the minimum temperature at which ethylene is decomposed, it was heated at a temperature varying from 350° to 375° for five hours. Slight decomposition was evident, for the gas contracted slightly, and its odor was changed altogether, being like that of impure kerosene. As the decomposition was evidently slow at this temperature, and a number of hours would be necessary for each experiment, a careful examination was made to see if the gas could be kept in the heating apparatus absolutely without leakage. It was filled with ethylene, and a portion drawn off and analysed by absorption; the apparatus, which was apparently air-tight, was then allowed to stand for

about twenty-four hours, and the gas then analysed again, from which it was seen that air had diffused through the rubber joints. After trying various devices it became evident that ethylene could not be kept in such an apparatus for the length of time required for an experiment of this kind without diffusion through the rubber. It was necessary, therefore, to arrange the apparatus without rubber joints, and for greater security, joints of all kinds were made unnecessary by the following arrangement (see Figure).



A tube of moderately hard glass about five feet long was bent twice at right angles, and the ends drawn out so as to allow rubber tubes to slip over them. These rubber tubes were connected with two open glass tubes, B and B'. Ethylene was passed through B until all the air was expelled from the whole apparatus; mercury was then poured into B and B' so that the gas was confined over mercury alone. By raising or lowering B or B', the pressure could be adjusted to that of the atmosphere, and any change in volume could be noticed at once by a change of the mercury level. The portion of the tube to be heated was enclosed in a

cylindrical air-bath of sheet iron, *A*. This was heated by a small gas furnace. Low temperatures were determined by a mercury thermometer; but as this could not be used for temperatures above 300°, and as it was impracticable to use the Siemens pyrometer in this apparatus, an air-thermometer of the form devised by Joly[1] was arranged with a specially constructed air bulb about eight inches long and one inch inner diameter; this was placed close beside the heating tube and both packed in asbestos.

In order to maintain constant temperature the following gas regulator was devised, and gave satisfactory results. A branch pipe *c*, from the gas-supply passed to the top of the air-thermometer and terminated in a fine glass jet, *d*, which dipped under the mercury in the manometer which indicates the pressure of the air-thermometer. The top of the manometer was then enclosed by a glass tube, so as to convey the gas by the tube *f* to the furnace. If the temperature of the thermometer bulb was lowered slightly, the mercury in the manometer sank and opened the jet from the branch tube *c*, sending an additional supply of gas to the furnace; by this means the temperature was raised again, until the branch supply was cut off by the rising mercury.

Ethylene, which by absorption analysis was 99.6 per cent. pure, was heated in this apparatus for seven and a half hours at 250°. On cooling the gas returned to its original volume, and there was no sign of change in constitution. The temperature was then raised to 275° and kept as near that point as possible for seven hours, and again no change in constitution was noticed. The same gas was then heated to 300° for fourteen hours with the same result. It had been noticed repeatedly before that on heating ethylene to 350° to 375° a marked change in odor accompanied the decomposition; this was not noticed in the gas heated to 300°, the odor remained that of pure ethylene. As a final proof that no change in constitution had taken place, the gas before and after heating was analysed by combustion.

Analysis of Ethylene Before Heating.

	Volume.	Press.	Temperature.	Volume reduced to 1 meter and 0°.
Volume taken for analysis,	73.2	.1372	22.0	9.29
Volume after adding air,	383.3	.4454	22.0	158.00
Volume after explosion,	367.4	.4094	22.5	139.00
Volume after absorption of CO_2,	345.7	.3801	25.0	120.40

[1] Poggendorff's Annalen der Physik und Chemie, Jubelband, 82.

Theoret. volume of CO_2	$= 9.29 \times 2 =$	18.58 vols.
Found volume of CO_2	$=$	18.60
Theoret. volume of water vapor	$=$	18.58
Found volume of water vapor	$=$	18.00

Analysis of Ethylene After Heating.

	Volume.	Press.	Temperature.	Volume reduced to 1 meter and 0°.
Volume taken for analysis,	70.1	.1451	20.0	9.48
Volume after adding air,	470.8	.5432	20.7	238.3
Volume after explosion,	461.5	.5132	22.0	219.2
Volume after absorption of CO_2,	440.8	.4878	21.2	199.7

Theoret. volume of CO_2	$= 18.96$ vols.
Found volume of CO_2	$= 19.7$
Theoret. volume of water vapor	$= 18.96$
Found volume of water vapor	$= 19.10$

The two analyses agree sufficiently to show that no change was effected by the heating.

Second Series of Experiments.

Ethylene was passed through the heating tube until an absorption analysis showed it to contain ethylene more than 99 per cent. pure. The volume occupied by the gas was then marked off on the tube and the temperature of the room noted by the air-thermometer. The air-bath was then raised to 317° and kept between 315° and 320° for five hours. On cooling no change in volume was noticed. The heating was continued at 328°, 338°, 344°, successively for several hours with the same result. A very slight contraction was noticed at the last temperature, but it was not observed again, and was probably due to a rise in temperature beyond 344°. The gas was then kept at 350° to 355° for eight hours; on cooling slight contraction in volume was evident. By heating for sixteen hours longer the contraction approximated one-twentieth of the whole gas. It amounted to seven cubic centimeters in all, and hence could be easily observed. On heating the gas further at this temperature no more contraction could be obtained. The gas now had the sharp, disagreeable odor noticed before. It was all absorbed by fuming sulphuric acid. No permanent gas, such as methane or hydrogen, remained. It is evident

that the condensation must have resulted from polymerisation of ethylene. It will be observed that a condensation of two or more molecules of a hydrocarbon of the ethylene series will yield a hydrocarbon of the same series. If, on the other hand, a hydrocarbon of any other series had been formed, then hydrogen or a saturated hydrocarbon must have been formed which would not have been absorbed by sulphuric acid. The change in the gas was so slight that it did not affect the results of a combustion analysis of the gas.

Ethylene which had been heated at 350° until no further change could be noticed was then heated to 358° for eight hours without further contraction. On heating at 375° contraction began again, and continued until the whole volume was reduced by one-fifteenth —*i. e.*, 150 cc. were reduced to 140 cc. The gas was still all absorbed by fuming sulphuric acid. On heating to 400° and maintaining the temperature between 400° and 408° for five hours, contraction continued slowly. As the contraction did not stop, the heating was continued for 171 hours, the last 70 hours being uninterrupted. The total change in volume was from 132 cc. to 63 cc. The gas did not contract further at 400°. During the first days of the heating a small trace of some liquid substance appeared in the cool part of the tube. It was colorless at first, but became brown as it increased in quantity, finally amounting to two or three drops. A qualitative examination of the residual gas showed that a part was absorbed by ordinary strong sulphuric acid. The remaining part was not absorbed even by fuming sulphuric acid. Thus no ethylene remained undecomposed.

Analysis of Residual Gas.

	Volume.	Press.	Temp.	Volume reduced to 1 meter and 0° C.
Volume of gas taken	253.2	.3059	7.0	75.5
Volume of gas after adding air	371.3	.4210	2.5	154.9
Volume of gas after absorption with H_2SO_4	346.5	.4110	7.5	139.3
Volume of gas taken for combustion	289.0	.3695	14.0	101.5
Volume of gas after adding oxygen	452.2	.5055	12.0	219.1
Volume of gas after explosion	344.5	.4117	13.2	135.3
Volume of gas after absorption of CO_2	261.3	.3309	11.5	82.9
Volume of gas after adding hydrogen	329.1	.3915	10.5	124.1
Volume of gas after explosion	216.7	.2946	10.5	61.5
Volume of gas after adding hydrogen	301.3	.3632	12.5	104.6
Volume of gas after explosion	255.2	.3287	12.5	80.2

Contraction = 136.2
CO_2 = 52.4
Nitrogen = 53.9

Since only part of the gas was taken for combustion, the volumes found must be multiplied by $\frac{189.3}{101.5}$ to correspond to the whole volume of gas which gives

Contraction = 192.8
CO_2 = 71.9
Nitrogen = 74.0

In transferring the original gas from the heating tube to the eudiometer 12.8 volumes of air were introduced, which subtracted from the total volume leave 62.7 volumes of the mixture of hydrocarbons to be considered in the analysis.

Volume of gas taken	= 75.5
Air in above gas	= 12.8
Mixture of hydrocarbons	= 62.7
Hydrocarbons absorbed by H_2SO_4	= 15.6
	47.1
Carbon dioxide obtained	= 71.9
Contraction	= 186.9

The volume of carbon dioxide is more than would have been produced by marsh gas and less than ethane would have furnished. It can represent a mixture of ethane with marsh gas or with hydrogen. By passing the gas over spongy palladium under the conditions recommended by Hempel it was shown that no hydrogen was present; the gas therefore seemed to be a mixture of 22.3 volumes methane and 24.8 volumes ethane.[1] The entire gas seemed to be composed, therefore, of

Hydrocarbons of C_nH_{2n} series, ...	15.6 vols.
Ethane, ...	24.8
Methane, ...	22.3
	62.7

The liquid formed during the heating combined very readily with bromine without any noticeable evolution of hydrobromic acid. The amount was too small for any further investigation except to show by Hofmann's[2] test that benzene was absent.

[1] Bunsen's gasometrische Methoden, p. 62.
[2] Annales de Chimie et de Physique, 2d series, **43**.

Ethylene was next heated for 102 consecutive hours at 450°. The contraction proceeded more rapidly than at 400°. After seventy-two hours the contraction ceased, and the volume remained constant for thirty hours. The original volume, 150 cc., was reduced to 84.2 cc. The liquid had the same characteristics as before; the tube was very slightly blackened.

Analysis of Residual Gas.

	Volume.	Press.	Temp.	Volume reduced to 1 meter and 0°C.
Volume of gas taken	250.8	.3114	12.0°	74.87
Volume after absorption with ordinary H_2SO_4	217.5	.2849	11.5	59.50
Volume after absorption with fuming H_2SO_4	217.5	.2849	11.5	59.50
Volume after adding oxygen	320.3	.3875	12.0	118.9
Volume after explosion	391.2	.4458	13.0	166.5
Volume after adding oxygen	578.9	.6325	16.0	347.7
Volume after explosion	401.1	.4549	16.0	172.4
Volume after absorption with KOH	287.7	.3564	17.0	96.5

Air was introduced in transferring from the heating apparatus to the eudiometer; its amount was determined by an independent analysis to be 19.2 volumes.

Original volume	= 74.87
Air	= 19.2
Mixture of hydrocarbons,	= 55.67
Hydrocarbons of C_nH_{2n} series	= 15.37
Mixture of methane and ethane	= 40.30

As in the former analysis it was shown that this mixture consisted of 35.6 volumes ethane and 4.7 volumes methane, or the whole residual gas contained

Hydrocarbons of C_nH_{2n} series, ...	15.37
Ethane, ...	35.6
Marsh gas, ...	4.7
	55.67

The effort was made to heat ethylene at 500°, but the air-thermometer bulb softened at this temperature. It was evident that the decomposition was different at this temperature, for the tube was blackened by a considerable deposit of charcoal.

The facts which this work has established are, 1. Ethylene undergoes change by the action of heat at a temperature very much lower than has been observed in previous investigations. 2. The temperature at which ethylene begins to alter in constitution is about 350°C. 3. The change at this temperature consists in condensation without the formation of members of any series of hydrocarbons having a different percentage of carbon and hydrogen from ethylene. The change is slow, requiring at least twenty hours before it ceases, and it is not then complete. 4. If ethylene is heated to 400° for a sufficient length of time it is entirely decomposed with formation of marsh gas, ethane and liquid products, which will be investigated further.

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PARA-NITRO-BENZOIC SULPHINIDE.

BY W. A. NOYES.

In the study of the oxidation of benzene derivatives with potassium ferricyanide I wished to include an ortho-sulphamide. The ease with which para-nitro-toluene is oxidised by the agent in question, and the fact that when treated with fuming sulphuric acid it readily yields an acid containing the sulphonic group ortho to the methyl, suggested the corresponding sulphamide as likely to be well suited for my purpose. As this sulphamide had never been oxidised, it was thought best to study first the product obtained by oxidising it with potassium permanganate. The sulphinide obtained has proved to be of rather unusual interest, and, together with the corresponding amido-sulphinide, throws considerable light upon the character of the sulphinides.

As Remsen[1] proposes to make a thorough study of the sulphinides, I will not discuss the bearing of the facts which I have discovered, but will simply state that they furnish a strong confirma-

[1] This Journal **6**, 260. The experiments here described were partly completed before that paper was published. In a letter to Professor Remsen, written in April of that year, I mentioned some of the results which I had obtained, and in his reply I first learned that he was engaged in an extended study of the sulphinides. He kindly informed me that the study of the sulphinide which I was working with should not be taken up in his laboratory.

tion of the opinion expressed by Remsen[1] that the more common and perhaps the only form of the salts of the sulphinides is $R<\begin{matrix}CO\\SO_2\end{matrix}>NM$, and not, as was at first supposed, $R<\begin{matrix}CO_2M\\SO_2NH_2\end{matrix}$. An examination of the analytical data for the salts of other sulphinides obtained by Remsen and his co-workers makes it seem probable that some of these, at least, were also of the first form, and not of the last.

Preparation of Para-nitro-ortho-toluene-sulphamide.

Para-nitro-ortho-sulpho-toluene was obtained essentially as described by Hart.[2] Fifty grams of para-nitro-toluene were put in a flask, and 200 grams of a strongly fuming sulphuric acid were added. The mixture grew warm spontaneously, and in a few minutes a solution was obtained from which no nitro-toluene was precipitated on pouring it into water. The whole was then poured into water, neutralised with chalk, and the filtrate from the precipitated calcium sulphate was evaporated to dryness, and the calcium salt obtained was dried at 150°.

It was found that merely triturating the calcium salt with phosphorous pentachloride, or even heating the two together in a porcelain dish, converted but a small portion into the sulphochloride. Accordingly, the calcium salt and an equal weight of the pentachloride were intimately mixed and put in a flask. The mixture was then heated by immersing the flask in a boiling water-bath for twelve hours. At the end of the time all lumps of the pentachloride had disappeared, and the contents of the flask had the consistency of thick cream. The contents of the flask were poured into water, and the sulphochloride, which, under these circumstances, was liquid and did not solidify on cooling, was separated from the acid solution with a separatory funnel. It was then converted into the sulphamide by warming with concentrated aqueous ammonia. The sulphamide was easily purified by boiling with bone-black and crystallising from hot water. The amide crystallises in fine needles, which usually have a slight yellow color, but which may be obtained perfectly white. It fuses at 186°–187° (uncor.).

The potassium salt of para-nitro-ortho-sulpho-toluene was also

[1] This Journal **6**, 262. [2] *Ibid.* **1**, 350.

prepared, and as I find no recorded analysis, I will give mine, and also a solubility determination. The analysis was as follows:

0.3701 gram of the salt gave 0.1236 gram K_2SO_4.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3K\\NO_2\end{cases}$.	Found.
K	15.29	14.97

6.29 grams of a solution saturated at 16° left on evaporation 0.1606 gram of the salt dried at 150°. Victor Meyer's method.

100 parts of water at 16° dissolve 2.62 parts of the salt.

Oxidation of Nitro-toluene-sulphamide.

Several experiments were tried for the purpose of finding the best conditions for oxidation. The following method was found to be the most satisfactory: 5 grams of the amide were put in a flask with 500 cc. of water, 1 gram of potassium hydroxide was added, and then 10 grams of potassium permanganate in separate portions, while the whole was heated by immersion in a boiling water-bath. The amide is not entirely oxidised by the ten grams of permanganate, but if more is added it seems to act fully as much on the product of oxidation as on the amide, and the yield of the former is scarcely increased. After the permanganate was completely reduced the solution was filtered from the oxide of manganese, and the filtrate was nearly neutralised or rendered slightly acid with sulphuric acid. This usually caused the separation of about two grams of the unoxidised amide, which was filtered off and used for a new oxidation. The chief object of the neutralisation was to prevent a decomposition which seemed to take place when the alkaline solution was evaporated. On evaporating the neutral solution, filtered from the precipitated amide, to a small bulk and allowing it to cool, a difficultly soluble salt separated, which proved to be *potassium anhydro-nitro-sulphamine-benzoate*. The same salt may be obtained when the oxidation is conducted without the addition of potassium hydroxide, but the yield is very much smaller. The salt was purified by boiling repeatedly with alcohol to remove some of the amide with which it was always mixed, and by recrystallising from water.

Para-nitro-benzoic Sulphinide.

When hydrochloric acid is added to a hot, concentrated solution of the potassium salt, para-nitro-benzoic sulphinide separates from the solution on cooling. Under these circumstances the sulphinide crystallises sometimes in small leaflets and sometimes in fine needles. Both fuse at 209° (cor.). On spontaneous evaporation of its solutions it crystallises in short, thick prisms which combine together in macles. It is difficultly soluble in cold water, though scarcely less soluble than its potassium salt. It is more easily soluble in hot water, rather difficultly soluble in alcohol, and only slightly soluble in ether. The sulphinide and its salts have an intensely bitter taste, reminding one of quinine. Benzoic sulphinide, it may be remembered, is remarkably sweet.[1] The amido-sulphinide to be described below is also very sweet. The analyses were made with two different specimens with the following results:

I. 0.1150 gram gave 0.1212 gram $BaSO_4$ (Liebig's method as modified by Keiser[2]).

II. 0.1439 gram gave 0.1468 gram $BaSO_4$ (Carius).

III. 0.1412 gram gave 0.1437 gram $BaSO_4$ (Carius).

	Calculated for $C_6H_3\begin{smallmatrix}\diagup CO\\ —SO_2\\ \diagdown NO_2\end{smallmatrix}>NH$.	Found.		
		I.	II.	III.
S	14.04	14.47	14.02	13.99

From the method of preparation para-nitro-benzoic sulphinide must have the structure $C_6H_3\begin{smallmatrix}\diagup CO\\ —SO_2\\ \diagdown NO_2\end{smallmatrix}>NH$ (1. 2. 4.)

Potassium Anhydro-nitro-sulphamine-benzoate,

$C_6H_3\begin{smallmatrix}\diagup CO\\ —SO_2\\ \diagdown NO_2\end{smallmatrix}>NK$, prepared as described above, crystallises from a hot solution in fine leaflets. The salt is easily soluble in warm water, but difficultly soluble in cold. In order to establish the composition of the salt beyond question, determinations of potassium, hydrogen and sulphur were made. The results were as follows:

I. 0.1568 gram of the salt gave 0.0507 gram K_2SO_4.

[1] This Journal **1**, 430.

[2] *Ibid.* **5**, 207.

II. 0.1866 gram of the salt gave 0.0606 gram K_2SO_4.

III. 0.3591 gram of the salt, burned with copper oxide, gave 0.0422 gram H_2O.

IV. 0.3443 gram of the salt gave, in the same way, 0.0403 gram H_2O.

V. 0.1387 gram of the salt gave 0.1187 gram $BaSO_4$ (Liebig).

VI. 0.1836 gram of the salt gave 0.1629 gram $BaSO_4$ (Liebig).

	Calculated for $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>NK$.	Found.						Calculated for $C_6H_3\begin{cases}CO_2K\\SO_2NH_2\\NO_2\end{cases}$.
		I.	II.	III.	IV.	V.	VI.	
K	14.66	14.50	14.56	...	...	...	...	13.73
H	1.13	...	...	1.31	1.30	...	...	1.76
S	12.03	...	...	...	...	11.75	12.18	11.27

A solubility determination was made with the following results: 8.83 grams of a solution saturated at 18.5° left on evaporation 0.0836 gram of the salt.

100 parts of water at 18.5° dissolve 0.96 part of the salt.

Barium Anhydro-nitro-sulphamine-benzoate,

$\left(C_6H_3\begin{cases}CO\\SO_2>N\\NO_2\end{cases}\right)_2Ba + 3H_2O$. This was obtained by boiling the nitro-sulphinide with barium carbonate and water. The solution of the salt was filtered from the excess of barium carbonate, evaporated somewhat and allowed to cool, when the salt separated in well-formed, short prisms which had a tendency to a concentric grouping. The salt has a bitter taste. The analyses were as follows:

I. 0.3783 gram of the salt lost 0.0322 gram H_2O at 145°.

II. 0.3361 gram of the salt lost 0.0288 gram H_2O at 145°.

	Calculated for $\left(C_6H_3\begin{cases}CO\\SO_2>N\\NO_2\end{cases}\right)_2Ba + 3H_2O$.	Found.	
		I.	II.
H_2O	8.37	8.51	8.57

The salt can be heated to 210° without decomposition.

I. 0.2835 gram of the anhydrous salt gave 0.1117 gram $BaSO_4$.

II. 0.3073 gram of the anhydrous salt gave 0.1211 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}CO\\SO_2>N\\NO_2\end{cases}\right)_2Ba$.	Found.		Calculated for $\left(C_6H_3\begin{cases}CO_2\\SO_2NH_2\\NO_2\end{cases}\right)_2Ba$.
		I.	II.	
Ba	23.18	23.17	23.18	21.85

Silver Anhydro-nitro-sulphamine-benzoate, $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>NAg$.

The silver salt of the sulphinide was prepared by precipitating a solution of the potassium salt with silver nitrate. The precipitated salt was washed thoroughly with cold water and dried by allowing it to stand for some time loosely covered with filter paper. It is almost insoluble even in boiling water. The salt contains no water of crystallisation. The analyses were as follows:

I. 0.1291 gram of the salt gave 0.0413 gram Ag.
II. 0.1549 gram of the salt gave 0.0498 gram Ag.
III. 0.2086 gram of the salt gave 0.0673 gram Ag.

	Calculated for $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>NAg$	Found.			Calculated for $C_6H_3\begin{cases}CO_2Ag\\SO_2NH_2\\NO_2\end{cases}$.
		I.	II.	III.	
Ag	32.24	31.99	32.15	32.26	30.59

Para-amido-benzoic Sulphinide.

Six grams of the potassium salt of the nitro-sulphinide were placed in a flask, and 15–20 cc. of concentrated ammonia were added. A rapid current of hydrogen sulphide was then passed into the mixture. Solution took place speedily with a considerable evolution of heat. The current of gas was continued for a few minutes longer, and the solution was then poured into a porcelain dish and evaporated to dryness on the water-bath. The residue was treated with water and filtered to remove the sulphur which had separated. On acidifying the filtrate with hydrochloric acid, para-amido-benzoic sulphinide separated mixed with some sulphur. It was purified by crystallising from water.

Para-amido-benzoic sulphinide, $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>NH$ $^{1,}_{2,}$ crystallises ^{4,} in fine needles, which usually have a slight yellow color. The color can be removed, however, by dissolving the substance in alcohol and pouring the solution into water. The sulphinide is almost insoluble in cold water, difficultly soluble in hot water, rather difficultly soluble in alcohol and ether. Its solution, even when very dilute, shows a beautiful dark blue fluorescence. It has an intensely sweet taste. When heated rapidly it fuses at 283°–285° (cor.), and immediately decomposes.

The portion used for the first analysis was obtained by crystallising once from hot water as described above. That used for the second analysis was obtained by acidifying a solution of the barium salt with hydrochloric acid and washing the precipitated sulphinide thoroughly with water. The results were as follows:

I. 0.1188 gram gave 0.1416 gram $BaSO_4$ (Carius).

II. 0.1470 gram gave 0.1735 gram $BaSO_4$ (Carius).

	Calculated for $C_6H_3{<}^{CO}_{SO_2}{>}NH$.	Found.	
		I.	II.
S	16.16	16.37	16.20

Potassium Anhydro-amido-sulphamine-benzoate,

$C_6H_3{<}^{CO}_{SO_2}{>}NK + H_2O$. A weighed portion of the amido-sulphinide was neutralised with the calculated amount of a standard solution of potassium hydroxide. The salt proved to be very easily soluble in water. On allowing the solution to evaporate spontaneously the salt was deposited on the sides of the beaker in a crust creeping nearly to the top. Under a glass the crust was seen to consist of fine needles. Portions of this crust lost water rapidly on standing over calcium chloride and became effloresced in appearance. The amount of water lost indicates that the salt prepared as described above contains eight molecules of water and loses seven molecules on standing over calcium chloride. Two determinations of the water lost over calcium chloride gave respectively 32.47 and 34.23 per cent. Theory requires for a salt containing eight molecules of water and losing seven, 33.16 per cent. Not much reliance is placed on the analyses, as there was not sufficient evidence of the purity of the salt. The salt is soluble with difficulty in cold alcohol of 90 per cent., but more easily soluble in hot alcohol. From the hot solution it separates, on cooling, in long, well-formed, fine needles, which contain one molecule of water. They are, however, hygroscopic, and retain, even while standing over calcium chloride, a small portion of hygroscopic moisture, so that the determinations of water do not agree well with the calculated amount. The same remark applies to the salt at first described. The first analysis given below was with the salt obtained by spontaneous evaporation of the aqueous solution. The other two analyses were with the salt crystallised from alcohol. Each salt was dried over calcium chloride.

I. 0.1044 gram of the salt lost 0.0088 gram H_2O at 140°.
II. 0.2447 gram of the salt lost 0.0211 gram H_2O at 140°.
III. 0.1351 gram of the salt lost 0.0109 gram H_2O at 150°.

	Calculated for $C_6H_3\begin{cases}CO\\SO_2\\NH_2\end{cases}>NK + H_2O$.	Found.		
		I.	II.	III.
H_2O	7.09	8.43	8.62	8.07

A portion of the salt which lost 8.30 per cent. of water at 150° regained a little *more* than it had lost on standing open in the laboratory over night. On heating for a half hour at 220° the salt turned slightly brown, but lost less than one-half of one per cent. in weight. The determinations of potassium were as follows:

I. 0.0956 gram of the anhydrous salt gave 0.0352 gram K_2SO_4.
II. 0.2236 gram of the anhydrous salt gave 0.0814 gram K_2SO_4.
III. 0.1242 gram of the anhydrous salt gave 0.0450 gram K_2SO_4.

	Calculated for $C_6H_3\begin{cases}CO\\NH_2\end{cases}>NK$.	Found.			Calculated for $C_6H_3\begin{cases}CO_2K\\SO_2NH_2\end{cases}$.
		I.	II.	III.	
K	16.53	16.50	16.35	16.26	15.35

Barium Anhydro-amido-sulphamine-benzoate,

$\left(C_6H_3\begin{cases}CO\\SO_2\\NH_2\end{cases}>N\right)_2Ba + 6H_2O$. This was obtained by boiling the amido-sulphinide with barium carbonate and a little water. On cooling the solution filtered from the excess of barium carbonate, the salt separated in fine needles. The salt is quite easily soluble in water. It has a sweet taste. Some difficulty was found in determining the water of crystallisation. In warm, dry weather the salt contains a little less water than theory requires for six molecules; in damp weather, on the contrary, the salt contains a little more than the calculated amount. When dried over calcium chloride the salt contains three molecules of water. The analytical results are as follows:

I. 0.3953 gram of the salt lost 0.0369 gram H_2O over $CaCl_2$.
II. 0.3875 gram of the salt lost 0.0358 gram H_2O over $CaCl_2$.

	Calculated for $\left(C_6H_3\begin{cases}CO\\SO_2\\NH_2\end{cases}>N\right)_2Ba + 6H_2O$.	Found.	
		I.	II.
$3H_2O$	8.45	9.33	9.24

I. 0.3584 gram of the salt dried over $CaCl_2$ lost 0.0330 gram H_2O at 160°.

II. 0.3517 gram of the salt dried over $CaCl_2$ lost 0.0324 gram H_2O at 160°.

	Calculated for $\left(C_6H_3\begin{matrix}CO\\SO_2\\NH_2\end{matrix}>N\right)_2Ba + 3H_2O$.	Found. I.	Found. II.
$3H_2O$	9.23	9.21	9.21

I. 0.2933 gram of the anhydrous salt gave 0.1282 gram $BaSO_4$.

II. 0.2086 gram of the anhydrous salt gave 0.0910 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{matrix}CO\\SO_2\\NH_2\end{matrix}>N\right)_2Ba$.	Found. I.	Found. II.	Calculated for $\left(C_6H_3\begin{matrix}CO_2\\SO_2NH_2\end{matrix}\right)_2Ba$.
Ba	25.80	25.67	25.65	24.16

Silver Anhydro-amido-sulphamine-benzoate,

$C_6H_3\begin{matrix}CO\\SO_2\\NH_2\end{matrix}>NAg + H_2O$. When silver nitrate is added to a solution of the barium salt, the silver salt separates as a white, amorphous precipitate. After washing thoroughly with cold water and drying in the air, this contains one molecule of water. The salt loses three-fourths of its water on standing for a day over sulphuric acid. It is soluble with difficulty in hot water, and crystallises from the solution, on cooling, in fine needles, which have a slight brown color. These lost less than one per cent. of water on heating to 170°. Hence the crystallised salt seems to be anhydrous. The analyses given below were with the precipitated, air-dry salt.

I. 0.1884 gram of the salt lost 0.0105 gram H_2O at 160° and gave 0.0622 gram Ag.

II. 0.2050 gram of the salt lost 0.0108 gram H_2O at 160° and gave 0.0690 gram Ag.

III. 0.2086 gram of the salt lost 0.0112 gram H_2O at 160° and gave 0.0702 gram Ag.

	Calculated for $C_6H_3\begin{matrix}CO\\SO_2\\NH_2\end{matrix}>NAg + H_2O$.	Found. I.	Found. II.	Found. III.	Calculated for $C_6H_3\begin{matrix}CO_2Ag\\SO_2NH_2\end{matrix} + H_2O$.
H_2O	5.56	5.69	5.27	5.37	5.28
Ag	33.45	33.74	33.66	33.65	31.67

An analysis of the crystallised salt, dried at 170°, gave 35.47 per cent. of Ag. Theory requires 35.41 per cent.

UNIVERSITY OF TENNESSEE, *November* 10, 1885.

ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.[1]

BY W. A. NOYES.

III.

Remsen and Fahlberg, in studying the oxidation of ortho-toluene-sulphamide with potassium permanganate, discovered the substance known as benzoic sulphinide. By oxidising the same sulphamide with potassium ferricyanide, I have, to my surprise, found that the chief product of the oxidation is not the sulphinide, but ortho-sulphamine-benzoic acid, the acid of which benzoic sulphinide is the anhydride. This is the first *ortho*-sulphamine acid ever prepared, as in all cases heretofore studied, where the oxidising agent has been potassium permanganate, sulphinides have been obtained, and it has seemed probable, for that reason, that a carboxyl-group could not exist in the ortho-position to a sulphamide-group. The experiments here described show that the two groups may exist in the ortho-position to each other, and that the formation of benzoic sulphinide depends, in part at least, upon the oxidising agent used in its preparation.

As much difficulty was experienced in obtaining the ortho-toluene-sulphamide used in the experiments, I will notice briefly the methods which were tried for its preparation. The portion used in the first experiments was prepared, as by Remsen and Fahlberg,[2] from the sulphonic acids obtained by the direct treatment of toluene with fuming sulphuric acid. The process is a very tedious one, and the yield is very poor. An attempt was next made to prepare it from para-nitro-toluene by the method described by Ascher.[3] The purest amide obtained in this way fused at 146°, and it was found impossible to purify it by crystallising it from alcohol or from a mixture of alcohol and ether. Finally, much more satisfactory results were obtained by the process described by Claesson and Wallin.[4]

150 grams of sulphuryl-hydroxyl chloride were put in a flask fitted with a drop-funnel and with a delivery-tube, which was connected with a wide tube that dipped just under the surface of water in a beaker. 60 grams of toluene were added slowly from the

[1] This Journal **7**, 145. [2] *Ibid.* **1**, 426, and **1**, 170. [3] Annalen **161**, 8. [4] Berichte **12**, 1848.

drop-funnel, while the flask was placed in cold water and shaken constantly to prevent the temperature from rising too much. After the toluene was all added the mixture was poured into cold water. In this way there were obtained directly, from 200 grams of toluene, 236 grams of the crude toluene-sulpho-chlorides. This process entirely avoids the tedious conversion of the sulphonic acids into the sulpho-chlorides through the calcium and potassium salts. The liquid sulpho-chloride was separated as completely as possible from the para-compound by cooling with a freezing mixture, and was then converted into the amide by treatment with aqueous ammonia. The amide was purified essentially as described by Remsen and Fahlberg,[1] except that after boiling several times with water the amide remaining undissolved was treated with chloroform to remove a dark, gummy impurity.

In recrystallising the amide it was found best to treat it with enough boiling water to bring it almost entirely into solution; on cooling the solution to about 70° and keeping it at that temperature for some time, while it is frequently stirred, most of the ortho-amide separates as a granular precipitate, while a mixture of ortho- and para-amides, which cannot be further separated by crystallisation, remains in solution, and can be separated from the ortho-amide by filtering hot. On recrystallising the ortho-amide separated in this way, it is usually perfectly pure. From 200 grams of toluene there were obtained 33 grams of the pure ortho-amide fusing at 155°.

Claesson and Wallin obtained, besides the ortho-toluene-sulph-amide, another amide fusing at 108°, which they considered as a meta-compound, although they were familiar with the work by which Fahlberg[2] showed that a similar amide obtained from the sulphonic acids formed, when toluene is treated directly with fuming sulphuric acid, is not meta-toluene-sulphamide, but a mixture of the ortho- and para-amides. As I obtained some of the same amide fusing at 108°–110°, it seemed of interest to determine whether it was in reality a meta-amide or not.

Seven grams of the amide were accordingly boiled for three-quarters of an hour with the usual oxidising mixture of potassium pyrochromate, sulphuric acid and water. Under these conditions both the para[3]- and meta[4]-amide yield the corresponding sulph-

[1] *Loc. cit.*
[2] This Journal **1**, 172.
[3] Remsen, Annalen **178**, 304.
[4] Remsen and Palmer, this Journal **4**, 142.

amine benzoic acids, while the ortho-amide is only slightly attacked. After cooling, the acid formed by the oxidation, together with some unoxidised amide, were filtered off and washed till the filtrate ran through colorless. The acid was then converted into the barium salt by boiling with barium carbonate. The filtrate from the excess of barium carbonate deposited, on cooling, about a gram of an amide which fused at 145°. On dissolving this in hot water and cooling the solution somewhat, an amide separated which fused at 154°; hence, was nearly pure ortho-toluene-sulphamide. The solution of the barium salt was evaporated to dryness, and the residue was treated several times with alcohol to remove the rest of the unoxidised amide. The salt was then recrystallised from water. The salt obtained in this way contained, after drying for three days over sulphuric acid, only 4.33 per cent. of water. The salt of the meta-acid contains, under these circumstances, four molecules of water,[1] which would require 11.82 per cent. The anhydrous salt gave 25.68 per cent. Ba. Theory requires 25.51 per cent. The acid separated from a portion of the crystallised salt fused, and instantly decomposed at 292°–294° (uncor.). The acid separated from the mother-liquors of the salt fused at exactly the same temperature. When heated slowly the acid fused and decomposed at about 280°. Meta-sulphamine-benzoic acid fuses at 246°–247°. (See the following paper.) Hence, the amide fusing at 108°–110° contains both the ortho- and the para-amides, and there is no evidence that it contains anything else. It is undoubtedly the same substance as the amide which was examined by Fahlberg with similar results.

Oxidation of Ortho-toluene-sulphamide.

The ortho-toluene-sulphamide was oxidised by boiling it in lots of 3 grams each, with 75 grams of potassium ferricyanide, 30 grams of caustic potash, and 300 cc. of water. The solutions obtained from several oxidations were united and concentrated by evaporation, and most of the potassium ferrocyanide was removed by crystallisation. Enough dilute sulphuric acid was then added to convert all of the potassium carbonate present into the acid carbonate. This precipitated most of the unoxidised amide along with a considerable quantity of potassium sulphate. The filtrate

[1] Remsen and Palmer, *loc. cit.*

from these was then made strongly acid and extracted with ether. The acid is removed from the solution with some difficulty, and it is necessary for that reason to repeat the extraction many times.

The ether was distilled, and the acids which remained were converted into the barium salts in the usual way. The solution was evaporated, and a syrupy residue was treated several times with alcohol to remove any of the unoxidised amide which it contained. The residue was dissolved in hot water and the solution evaporated somewhat. On cooling, a rather difficultly soluble salt was deposited in well-formed, thick needles, which had a strong tendency to a concentric grouping. They were perfectly white in color. In order to insure perfect purity the crystals were air-dried, and then, after pulverising them finely, they were treated several times with ether. The salt was then recrystallised from water as before.

Ortho-sulphamine-benzoic Acid.

Two grams of the salt last mentioned were dissolved in hot water, and the solution was acidified with hydrochloric acid. On cooling, an acid separated in fine needles. In another case, when a mixture of the barium salts of benzoic sulphinide and of ortho-sulphamine-benzoic acid was acidified, the sulphinide separated almost immediately as a granular precipitate, while the acid separated slowly on allowing the solution to stand for several days in a cool room. Under these circumstances the acid was composed of quite large, clear, prismatic crystals which appeared to belong to the monoclinic system. The acid is quite readily soluble in cold water, easily soluble in alcohol and ether. It has a pleasant acid taste, but is not sweet. A little of the alcoholic solution, when evaporated spontaneously on a watch-glass, leaves a syrupy residue. The alcoholic solution of benzoic sulphinide evaporated in the same way leaves a dry residue. The ethereal solutions act in much the same way, but in that case the acid soon begins to crystallise at some point, and solidification then proceeds radially to the edges.

When heated rapidly the acid fuses at 165°–167°. If heated slowly it fuses at 153°–155°, apparently owing to its partial conversion into benzoic sulphinide, for, if it is kept at that temperature for a short time, it becomes solid again, and may then be heated to 210° before it will fuse a second time. The substance in the tube then has the intensely sweet taste which is so characteristic of

benzoic sulphinide. Pure benzoic sulphinide fusing at 223°–224° (uncor.) was also obtained by heating a portion of the acid to 180° in an air-bath, and recrystallising from water a dark residue which remained in the crucible. That the change is due to a loss of water of constitution and not of crystallisation, is proved by the fact that the salts of the sulphinide are totally distinct from the salts of the acid. For analysis the acid was dried for a short time at 95°.

I. 0.1191 gram of the acid gave 0.1386 gram $BaSO_4$.

II. 0.1132 gram of the acid gave 0.1310 gram $BaSO_4$.

III. 0.1059 gram of the acid gave 0.00730 gram N.

	Calculated for $C_6H_4<^{COOH}_{SO_2NH_2}$.	Found.		
		I.	II.	III.
S	15.92	15.98	15.89	...
N	6.97	...	...	6.89

Barium Ortho-sulphamine-benzoate,

$\left(C_6H_4<^{CO_2}_{SO_2NH_2}\right)_2Ba + 9H_2O$. This was prepared and purified as described above. When deposited on cooling a warm solution, the salt has the composition given here. On standing over calcium chloride for a day it loses seven molecules of water. The other two molecules are given off slowly at 111°, and more rapidly at 125°. The anhydrous salt is not sweet, but if it is heated to 130° or above it becomes sweet, owing, apparently, to a partial conversion into the corresponding salt of benzoic sulphinide. The salt of benzoic sulphinide was, for the purpose of comparison, prepared essentially as described by Remsen and Fahlberg,[1] except that greater care was taken to completely remove any of the unoxidised amide which it contained. It was found that the barium salt of the sulphinide is isomeric with the salt of the acid when the latter is dried over calcium chloride, but the two salts are not identical. The salt of the sulphinide is sweet in taste; that of the acid is not. The salt of the acid loses *two* molecules of water at 125°; that of the sulphinide loses *four* molecules at the same temperature, and then has the composition $\left(C_6H_4<^{CO}_{SO_2}>N\right)_2Ba$. The analysis of the salt gave 12.66 per cent. H_2O and 23.59 per cent. Ba. Theory requires 12.56 per cent. H_2O and 23.91 per cent. Ba.

[1] This Journal **1**, 428.

When a solution of pure barium ortho-sulphamine-benzoate is evaporated on the water-bath, it deposits, when very concentrated, a salt which crystallises in well-formed prisms or thick needles, and which contains two molecules of water.

The analyses of the salts were as follows:

I. 0.2990 gram of the salt deposited from the cold solution lost 0.0538 gram H_2O over $CaCl_2$.

II. 0.1654 gram of the same salt lost 0.0279 gram H_2O.

	Calculated for $\left(C_6H_4<\begin{matrix}CO_2\\SO_2NH_2\end{matrix}\right)_2Ba + 9H_2O$.	Found. I.	Found. II.
$7H_2O$	18.03	17.99	16.87

The salt loses its water very easily, and it is probable that the portion used for the second analysis was slightly effloresced, though it had been kept in a corked vial. Analyses I and II following were made with the salt deposited from a cold solution and dried over calcium chloride. Analysis III was made with a salt obtained by evaporating the solution to crystallisation on a water-bath.

I. 0.2452 gram lost 0.0145 gram H_2O at 125° and gave 0.0998 gram $BaSO_4$.

II. 0.1375 gram lost 0.0088 gram H_2O at 125° and gave 0.0557 gram $BaSO_4$.

III. 0.2905 gram gave 0.1185 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{matrix}CO_2\\SO_2NH_2\end{matrix}\right)_2Ba + 2H_2O$.	Found. I.	Found. II.	Found. III.
$2H_2O$	6.28	5.91	6.40	...
Ba	23.91	23.94	23.82	23.99

Di-silver Ortho-sulphamine-benzoate, $C_6H_4<\begin{matrix}CO_2Ag.\\SO_2NHAg.\end{matrix}$

When silver nitrate is added to a warm solution of the barium salt, a small amount of a salt containing two atoms of silver in the molecule separates at once. If this is filtered off, the slightly acid solution deposits, on cooling, the normal salt containing but one atom of silver in the molecule. The former salt may be obtained in larger quantity by adding to a weighed portion of the acid a little less than twice the amount of ammonia necessary to form the normal ammonium salt. On adding silver nitrate the salt separates as an amorphous precipitate, which becomes crystalline on

heating. The salt may be crystallised from hot water, and is then composed of fine leaflets. Both silver salts lose in weight and become sweet in taste on heating to 170°–180°, evidently through a partial conversion into the corresponding salt of the sulphinide. Analysis I was with the salt precipitated from the normal barium salt. The salt for the second analysis was prepared from the barium salt and silver nitrate, with the addition of a little ammonia. The salt was recrystallised from water. The salt for the third analysis was prepared from the acid by adding to it nearly twice the amount of ammonia necessary to form the normal salt, and precipitating with silver nitrate.

I. 0.0232 gram of the salt gave 0.0121 gram Ag.

II. 0.1063 gram of the salt gave 0.0550 gram Ag.

III. 0.1153 gram of the salt gave 0.0596 gram Ag.

	Calculated for $C_6H_4<^{CO_2Ag}_{SO_2NHAg}$.	Found.		
		I.	II.	III.
Ag	52.05	52.16	51.74	51.69

Mono-silver Ortho-sulphamine-benzoate,

$C_6H_4<^{CO_2Ag}_{SO_2NH_2}$. This is prepared best by adding to the acid a little less than enough ammonia to form the normal salt, and silver nitrate. The salt crystallises in fine, feathery needles. It is much more easily soluble than the di-silver salt. The analyses were made with salts of different preparations.

I. 0.1044 gram of the salt gave 0.0371 gram Ag.

II. 0.0344 gram of the salt gave 0.0119 gram Ag.

III. 0.1024 gram of the salt gave 0.0357 gram Ag.

	Calculated for $C_6H_4<^{CO_2Ag}_{SO_2NH_2}$.	Found.		
		I.	II.	III.
Ag	35.06	35.54	34.59	34.86

Silver Salts of Para-sulphamine-benzoic Acid.

As the silver salts of the sulphamine acids have been little studied, it seemed of interest to see if other salts similar to the first described above could be prepared. At my suggestion Mr. Chas. Walker has prepared and analysed the corresponding salts of para-sulphamine-benzoic acid. The salts were prepared from the ammonium salt essentially as described above. Both salts

are very difficultly soluble even in hot water, and they were not recrystallised. The analyses were as follows:

I. 0.2022 gram of the normal salt gave 0.0709 gram Ag.

II. 0.2210 gram of the normal salt gave 0.0774 gram Ag.

	Calculated for $C_6H_4<^{CO_2Ag}_{SO_2NH_2}$.	Found. I.	Found. II.
Ag	35.06	35.06	35.02

I. 0.2075 gram of the di-silver salt gave 0.1079 gram Ag.

II. 0.2220 gram of the di-silver salt gave 0.1155 gram Ag.

	Calculated for $C_6H_4<^{CO_2Ag}_{SO_2NHAg}$.	Found. I.	Found. II.
Ag	52.05	52.00	52.03

While, so far as I am aware, silver salts of the nature of those last described have never been prepared before, compounds of a similar nature have been known for many years. Thus, Anna Wolkow[1] prepared from para-toluene-sulphamide a potassium salt of the formula $C_6H_4<^{CH_3}_{SO_2NHK}$. Gerhardt[2] also refers to silver and mercury salts of similar amides, and shows very clearly in the article referred to that an ammonia residue is either basic or acid in nature, according to the character of the radical or radicals with which it is combined. The effect of an acid radical in giving strong acid properties to an ammonia residue is especially marked in the sulphinides. Strong acids are also formed in some other cases where two of the hydrogen atoms of ammonia are replaced by acid radicals.

The silver salt of benzoic sulphinide was also prepared, for the purpose of comparison, by adding silver nitrate to a solution of its barium salt and crystallising from hot water. It is composed of fine needles, with no tendency to a concentric grouping. It is sweet in taste.

I. 0.1839 gram of the salt gave 0.0683 gram Ag.

II. 0.1139 gram of the salt gave 0.0421 gram Ag.

	Calculated for $C_6H_4<^{CO}_{SO_2}>NAg$.	Found. I.	Found. II.
Ag	37.24	37.14	36.97

Remsen and Fahlberg[3] found that when ortho-toluene-sulphamide is oxidised by potassium permanganate, benzoic sulphinide

[1] Berichte **3**, 424. [2] Annalen **87**, 298. [3] *Loc. cit.*

and sulpho-benzoic acid are formed in nearly equal amounts. The same substances are formed, but in comparatively small quantity, when the oxidation is effected by potassium ferricyanide.

After most of the barium ortho-sulphamine-benzoate obtained by boiling the ethereal extract mentioned in the earlier part of this paper with barium carbonate had been crystallised out, the mother-liquors were acidified with hydrochloric acid. A small portion of benzoic sulphinide separated almost immediately as a granular precipitate. On allowing the solution to stand for some time in a cold room a considerable quantity of ortho-sulphamine-benzoic acid separated in quite large, clear crystals. After filtering off, washing and drying, these were easily separated mechanically from the sulphinide. The sulphinide was characterised by its intensely sweet taste, its melting-point of 220°–222° (uncor.), and by its silver salt, which was prepared and analysed. 0.2148 gram of the salt gave 0.0799 gram Ag, which corresponds to 37.19 per cent. Theory requires 37.24 per cent.

For the purpose of determining if any sulpho-benzoic acid was formed by the oxidation, to the solution which had been extracted with ether (see page 179) there was added a solution of ferric sulphate to precipitate the hydro-ferrocyanic acid. The excess of iron in the filtrate from the Prussian blue was precipitated with caustic potash, and to the filtrate from the ferric hydroxide was added enough more caustic potash to expel all ammonia from the solution. After the ammonia was expelled by evaporation, the excess of potassium hydroxide was exactly neutralised with sulphuric acid, the solution was evaporated, and most of the potassium sulphate was removed by crystallisation. The mother-liquors were then evaporated to dryness, and the residue was treated several times with strong alcohol. This seems to have dissolved chiefly potassium ortho-sulphamine-benzoate, and no evidence of the existence of sulpho-benzoic acid in the alcoholic solution could be obtained. The residue insoluble in alcohol was treated several times with a little water, and potassium sulphate was crystallised as far as possible from the solution. Finally the solution was concentrated to about 2 cc., and 3 cc. of strong alcohol were added. The precipitated potassium sulphate was filtered off and the filtrate was evaporated to dryness. The residue was taken up with a very little water, and the solution was acidified with hydrochloric acid. On evaporating over sulphuric acid a few crystals were deposited

in clear, well-formed plates. The properties of these agreed, as well as could be judged, with those of the acid potassium salt of ortho-sulpho-benzoic acid as described by Remsen and Fahlberg. The composition was confirmed by analysis. 0.0149 gram of the salt gave 0.0053 gram K_2SO_4, which corresponds to 15.97 per cent. of K. Theory requires 16.25 per cent.

Both benzoic sulphinide and ortho-sulpho-benzoic acid seem to be formed only in very small quantity when the oxidation of ortho-toluene-sulphamide is effected by means of potassium ferricyanide. The chief product of the oxidation is ortho-sulphamine-benzoic acid.

For the purpose of making an approximate estimate of the yield obtained by oxidation, one gram of ortho-toluene-sulphamide was oxidised in the usual manner. After removing most of the potassium ferrocyanide by crystallisation, the unoxidised amide was mostly precipitated by adding enough dilute sulphuric acid to convert the potassium carbonate present into the acid carbonate. The filtrate was then rendered strongly acid and extracted repeatedly with ether. The acids remaining after distilling off the ether were converted into the barium salts, and the barium in these was determined by precipitation as barium sulphate. 0.34 gram of barium sulphate was obtained, which would correspond to 0.59 gram of ortho-sulphamine-benzoic acid. The method given necessarily leaves out of consideration the ortho-sulpho-benzoic acid which is formed, and hence the actual amount of the acids formed must be somewhat greater than the weight given.

One gram of para-toluene-sulphamide treated in essentially the same way gave 0.46 gram of barium sulphate, which corresponds to 0.80 gram of para-sulphamine-benzoic acid. It seems probable from these figures that, as with the nitro-toluenes and the brom-toluenes, the para-amide is a little more easily oxidised than the ortho-compound.

OXIDATION OF META-BROM-TOLUENE.

By W. A. Noyes and Charles Walker.

In the experiments described in a previous paper it has been shown that meta-nitro-toluene conducts itself very differently from either ortho- or para-nitro-toluene when oxidised by potassium

ferricyanide. It was of interest, therefore, to study the action of the same agent upon other meta-compounds.

Meta-brom-toluene was prepared from para-acettoluid essentially as described by Grete.[1] 30 grams of para-acettoluid were dissolved in 25 grams of glacial acetic acid and one molecule of bromine was added slowly from a drop-funnel. The brom-acettoluid was precipitated by pouring the solution into water, and was recrystallised from alcohol. The acetyl-group was eliminated by boiling with alcoholic potash, and the brom-toluidine was distilled with water-vapor. It was then dissolved in absolute alcohol and a rapid stream of nitrous acid was passed into the solution. After distilling off the alcohol the meta-brom-toluene was distilled with water-vapor. It was purified by washing with dilute acid and alkali, and finally by distilling again with water-vapor from dilute sulphuric acid.

The oxidation was effected in the usual way by boiling 1 gram of the meta-brom-toluene with 25 grams of potassium ferricyanide, 10 grams of caustic potash and 100 cc. of water. After distilling the unoxidised brom-toluene with water-vapor, filtering, and crystallising out most of the potassium ferrocyanide formed, the solution was acidified and extracted with ether. The residue after distilling the ether was dissolved in a little ether and the solution was evaporated spontaneously. The residues from three oxidations, after drying over sulphuric acid, weighed respectively 0.0121, 0.0112 and 0.0111 gram.

To establish the identity of the acid the residues from several oxidations were boiled with barium carbonate. The barium salt obtained was purified by boiling with bone-black. The acid was then precipitated with dilute hydrochloric acid. It fused at 153.5°.

A comparison with the results obtained in the oxidation of ortho- and para-brom-toluene[2] shows that meta-brom-toluene is a little more easily oxidised than either of those. The amount of the compound oxidised is, however, exceedingly small in each case.

Oxidation of Meta-toluene-sulphamide.

The amide for the oxidation was prepared from pure ortho-brom-toluene. This was prepared from pure ortho-toluidine, partly by the method of Jackson,[3] and partly by that of Sand-

[1] Annalen **177**, 231. [2] This Journal **7**, 146. [3] *Ibid.* **1**, 100.

meyer.[1] In executing the latter method 12.5 grams of crystallised copper sulphate, 36 grams of potassium bromide, 20 grams of thin sheet copper, 11 grams of concentrated sulphuric acid, and 80 cc. of water were boiled in a flask with an inverted condenser until the reduction to cuprous bromide was complete and the solution became colorless. 10.7 grams of ortho-toluidine were then added, and, after heating nearly to boiling, a solution of 8.8 grams of potassium nitrite in 40 cc. of water was added slowly from a drop-funnel. The ortho-brom-toluene was then distilled from the solution with water-vapor and purified in the usual way. The yield was poor, but about the same as by the method of Jackson. As the previous preparation of hydrobromic acid is avoided, Sandmeyer's method is much easier of execution. Sandmeyer has found the yield poor in the case of other ortho-compounds, and thinks it, possibly, a general law that the reaction does not work smoothly in such cases.

10 grams of the pure ortho-brom-toluene were converted into the sulphonic acid by dissolving in 30 grams of fuming sulphuric acid. The sodium salt was prepared in the usual way. For the elimination of the bromine a method used by Sandmeyer[2] in a similar case was tried and found to work excellently. The solution of the sodium salt was evaporated to about 200 cc., and 100 cc. of a ten per cent. solution of caustic soda were added. The whole was then boiled gently for two hours with 15 grams of zinc dust. At the end of the time the organic salt in solution was found to be entirely free from bromine. The solution was filtered and nearly neutralised with sulphuric acid, which caused the precipitation of the zinc on boiling for a short time. The filtrate from the zinc hydroxide was evaporated to about 150 cc., and 65 cc. of strong alcohol were added. This caused the separation of most of the sodium sulphate. The filtrate was evaporated to dryness, and the sodium salt of the sulphonic acid was separated still more completely from the sodium sulphate by dissolving it in strong alcohol and filtering. The filtrate was evaporated to dryness, and the residue was treated with an equal weight of phosphorous pentachloride. When the action was complete the mixture was poured into water, and the sulpho-chloride, which fell to the bottom, was separated from the solution by use of a drop-funnel. It was then converted into the sulphamide by treatment with

[1] Berichte **17**, 2652. [2] *Ibid.* **18**, 1496.

strong aqueous ammonia. The sulphamide was boiled with bone-black and crystallised from water. It then fused at 90°–91°. Its purity was also established by analysis. 0.1210 gram gave 0.1652 gram $BaSO_4$, which corresponds to 18.74 per cent. of S. Theory requires 18.71 per cent.

The method described above for the elimination of bromine seems to be quite generally applicable, and is much quicker and easier of execution than the method where sodium amalgam is used. The method has also been applied successfully in the preparation of ortho-toluene-sulphamide from para-brom-toluene. It seems probable that potassium hydroxide might be substituted with advantage for sodium hydroxide, as potassium sulphate is much more easily removed from a solution than sodium sulphate.

The oxidation of the meta-toluene-sulphamide was effected in the usual way. The yield was determined as in the oxidation of ortho-toluene-sulphamide (see page 185). Two experiments gave respectively 0.43 and 0.44 gram $BaSO_4$, which correspond to 0.74 and 0.76 gram of meta-sulphamine-benzoic acid. After filtering the barium sulphate the acid in the filtrate was reconverted into the barium salt by boiling with barium carbonate. The salt was purified by evaporating the solution to dryness and treating the residue several times with strong alcohol to remove any of the unoxidised amide which it contained. It was then dissolved in water, the acid was precipitated with hydrochloric acid and recrystallised from hot water. Purified in this way it fused at 246°–247° (uncor.). Palmer[1] gives the fusing-point at 235°. In order to reconcile the discrepancy a small portion of the amide was oxidised with potassium permanganate exactly as described by him. By using the precautions mentioned above to insure purity, an acid was obtained which fused at 246°–247° as before. Palmer's acid was probably contaminated with a trace of the amide which could not be removed by recrystallising from water. The identity of the acid was also established by analysis. 0.1187 gram gave 0.1374 gram of $BaSO_4$, which corresponds to 15.89 per cent. of S. Theory requires 15.92 per cent.

The di-silver salt of the acid was also prepared in the manner described for the ortho- and para-acids. The salt forms an amorphous precipitate, and seems to separate again in the amorphous form when its solution in hot water has cooled. The analyses gave

[1] This Journal **4**, 144.

51.61 per cent. and 51.50 per cent. Theory requires 52.05 per cent.

There is completed, with the experiments here described, a systematic examination of three classes of toluene derivatives with reference to their conduct when oxidised by potassium ferricyanide in alkaline solution. The results obtained are summarised in the table given below. The numbers indicate the weight in grams of the substituted benzoic acid obtained when one gram of each substance is oxidised with 25 grams of potassium ferricyanide.

Toluene,	0.0090
Ortho-nitro-toluene,	0.69
Meta-nitro-toluene,	0.052
Para-nitro-toluene,	0.73
Ortho-brom-toluene,	0.0044
Meta-brom-toluene,	0.0115
Para-brom-toluene,	0.0065
Ortho-toluene-sulphamide,	0.59 +
Meta-toluene-sulphamide,	0.75
Para-toluene-sulphamide,	0.80

No great accuracy can be claimed for these numbers, of course, and in the case of ortho-toluene-sulphamide the result is known to be too low. However, the results are sufficiently accurate to give an answer to the question which was stated at the beginning of the investigation,[1] so far as toluene derivatives are concerned. Potassium ferricyanide conducts itself in the same manner as potassium permanganate in its ability to oxidise ortho-derivatives. Its conduct in this respect is totally different from that of chromic acid. No support is given, however, to that portion of Richard Meyer's[2] statement of Remsen's law which declares that ortho-groups are more easily oxidised than meta- or para-groups by an alkaline oxidising agent, except in the single case of meta-nitro-toluene. That case seems to be a somewhat anomalous one, and has been discussed in a previous paper. The para-compound seems, in each case, to be oxidised a little more easily than the ortho-compound, but the differences are insignificant.

The difficulty with which the bromine derivatives and toluene

[1] This Journal **5**, 99.

[2] Aromatische Verbindungen, 179.

itself are oxidised seems to be due, partly at least, to their almost total insolubility. The nitro-toluenes are appreciably soluble in hot water, and for that reason come much more intimately into contact with the oxidising agent. The sulphamides are completely dissolved in the solution which is used for their oxidation, and each of them is quite easily oxidised.

Apart from giving a partial answer to the question in consideration of which these investigations were originally commenced, the facts of most interest which have been brought out thus far are the anomalous conduct of meta-nitro-toluene, and the formation of ortho-sulphamine-benzoic acid, instead of benzoic sulphinide, which was expected. It is intended next to take up the study of some xylene derivatives for the purpose of determining, if possible, whether these facts are general in their application.

UNIVERSITY OF TENNESSEE, *April* 6, 1886.

NEW APPARATUS FOR THE ESTIMATION OF CARBONIC ACID IN THE AIR.

BY THOMAS C. VAN NÜYS.

From results of the estimation of carbonic acid in the air since Pettenkoffer[1] published his method, it is evident that either the amount of carbonic acid in the air varies greatly at different times or the methods employed are defective. Later investigations tend to prove that the methods are not reliable, the estimations being too high. Truchot's[2] maximum quantity found in forty-nine estimations made during fine weather was 4.2 volumes in 10,000 volumes of air, and where the ground was covered with snow his maximum quantity was 8.7 volumes. H. and A. Schlaginweit[3] found from 3.2 to 5.8 volumes in 10,000 volumes of air, according to altitude. Mène[4] found 7 volumes in 10,000 volumes of air. On the contrary, G. F. Armstrong[5] claims that the quantity of

[1] Sitzungsberichte der K. bayerischen Acad. d. Wissenschaft, 1860, 291.
[2] Ann. agronomiques, 1877, 69.
[3] Pogg. Annalen **76**, 442.
[4] Ann. de la société des sciences industrielles de Lyon, Nos. 1-9, in Rep. Chim. App. IV, 473.
[5] Proceedings Royal Society **30**, 343.

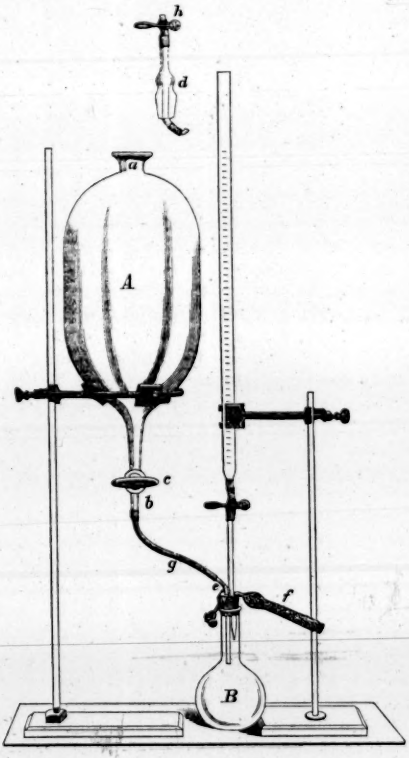
carbonic acid in the air does not exceed 3.5 volumes in 10,000 volumes of the air, and J. Reiset's[1] maximum quantity in ninety-one estimations was 3.415 volumes in 10,000 volumes of air, the average number of volumes being 2.978. Generally considered, the methods for the estimation of carbonic acid in the air, whether by passing air through tubes containing a solution of barium hydrate, or by shaking up a definite quantity of a standardised solution of barium hydrate with a measured quantity of air, do not provide sufficiently for preventing of contact of the external air containing CO_2 with the $Ba(OH)_2$ when titurated with oxalic acid or when filtered and washed.

By the apparatus illustrated by the figure it is intended to overcome this difficulty. The capacity of the apparatus *A*, ascertained by having determined its weight when empty and dry, and its weight when filled with distilled water at 4° C., is 6177 cc. The diameter of the mouth *a* of the apparatus is from 22.5 to 25 mm. The inside diameter of the end *b* of the apparatus is 65 mm. This drawn out, part of the apparatus is provided with a glass stop-cock *c*. The stopper *d* fits in the mouth of the apparatus by a ground surface so as to be perfectly air-tight. A hole 4.5 mm. in diameter passes through the stopper closed above by the rubber tube, and below the stopper is drawn out so as to form a tube which is bent and is connected to a piece of glass tubing by means of a rubber tube. The attached piece of tubing is bent upwards and drawn out so its orifice is 4 mm. in transverse diameter and 1.5 mm. perpendicular diameter.

When the stopper is in place, with a small quantity of grease it can be readily turned with the thumb and one finger. The capacity of the flask *B* is 400 cc., and it is provided with a rubber stopper having three holes. Through one of these holes passes the bent glass tube *e*, which is connected with the apparatus; through another hole the tip or dropper of the burette, and through the third hole the bent end of the chlor-calcium tube *f*. This tube is filled with pieces of pumice saturated with a strong solution of natr. hydrate. In estimating the carbonic acid in the air with this apparatus I use a solution of oxalic acid standardised according to Pettenkoffer,[2] and a solution of barium hyd. of one-half the strength of that of Pettenkoffer, thereby avoiding an excess of barium oxalate which makes the disappearance of the

[1] Comptes Rendus **90**, 1144. [2] Annalen der Chemie, Suppl. Band **2**, 25.

red color of the rosolic acid more obscure. 2.8636 grams pure oxalic acid which has neither effloresced nor deliquesced are dissolved in 1000 cc. distilled water. 1 cc. of this solution has the



same saturating power as 1 milligram CO_2. About 3.5 grams pure barium hydr. and .5 gram barium chlor. are dissolved in 1000 cc. water. If the solution is not clear it should be filtered. The

solution should be kept in an aspirator bottle, the stopper of which is connected with a large chlor-calcium tube having its end bent, and the tube filled with pieces of pumice saturated with a strong solution of natr. hydrate. In titurating the Ba hydr. solution with the solution of oxalic acid, contact with the external air is avoided by employing Pettenkoffer's[1] method in filling a pipette. The flask *B* may be employed in this tituration. Two or three drops of an alcohol solution of rosolic acid are introduced into it, the rubber tube *g* is removed from the end of the apparatus and is connected with a wash-bottle containing a solution of natr. hydrate, and a U-shaped tube containing soda-lime. The end of the chlor-calcium tube *f* is connected with an aspirator bottle filled with water, and air is drawn through the apparatus until the flask is filled with air free of CO_2. The end of the rubber tube *g* is taken between the thumb and finger and carefully disconnected and placed over the tip or dropper of a 50 cc. pipette containing the Ba solution, and when the solution has run into the flask, the end of the tube is removed from the pipette with the precaution that no outside air enter the tube. It is fitted over the mouth-piece of a wash-bottle filled with water.[2] About 100 cc. water is passed into the flask through the rubber tube, when it is secured by the pinch-cock. The oxalic acid solution is added until the red color disappears. Titurations should be repeated until an agreement is reached. As the oxalic acid solution is liable to change, titurations should be made every two or three days to avoid the uncertainty of results owing to decomposition of the acid in solution.

The stopper *d* is prepared for use by filling the canal passing through its entire length with water as a pipette is filled when the rubber tube is secured by the pinch-cock. The ground surface of the stopper is then rubbed with grease.

The inside surface of the apparatus *A* is dried, either by washing with absolute alcohol and ether, and let remain open in a warm place until dry, or by attaching the tube *b* to a foot-bellows by means of a rubber tube, and pumping air into it until dry. In this way the apparatus is filled with the air, the CO_2 of which it is intended to estimate.

[1] Mohr's Titrirmethode, Vierte Auf., 140.

[2] Every case in which water is used which will subsequently come in contact with the Ba solution, distilled water having been boiled is employed.

The flask *B* is dried, and into it are put two or three drops of an alcohol solution of rosolic acid. Air is introduced into it having its carbonic acid separated as before, when the rubber tube *g* is secured by the pinch-cock.

The apparatus having been filled with the air, the carbonic acid of which it is intended to estimate, a thermometer is suspended in the apparatus and let remain thirty minutes, so the temperature may become constant, when the temperature and barometric pressure are noted. 50 cc. of the barium solution are introduced into the apparatus *A*, the glass stop-cock having been closed. The stopper is put in place and secured by means of a rubber band. The apparatus *A* is turned on its side, placed on a table, and by frequent turning the inside surface is kept wet with the solution, and after the lapse of two hours all of the carbonic acid will have been absorbed. The lower end of the apparatus is raised a short distance from the table and the tube *b* is filled with water from the glass stop-cock to the end. The apparatus is returned to its place on the stand, the water remains in the tube, and the end of the rubber tube *g*, which is attached to the glass tube *e*, is filled with water from the part of tube secured by the pinch-cock to the end and fitted over the tube *b*, carefully excluding any air. The pinch-cock is removed to its place, as shown in the figure, and the glass stop-cock is carefully turned. If the air in the apparatus is under less pressure than the outside air, bubbles will pass through the barium solution into the apparatus, in which case the stop-cock should be turned so that the air may pass into the apparatus slowly and all the carbonic acid of the air be absorbed as it comes in contact with the natr. hydrate solution in the chlor-calcium tube. In a short time all of the barium hydrate solution will have passed into the flask. The rubber band or cord which secured the stopper in place is removed. An aspirator bottle containing water is placed one metre above the apparatus, and by means of a rubber tube 6 mm. internal diameter, connection is made between it and the rubber tube *h* attached to the stopper and secured by the pinch-cock. The rubber tubing making this connection should be filled with water to the exclusion of any air. As the pinch-cock is removed from the rubber tube at the stopper the water will flow into the apparatus and is thrown against its surface. By means of the thumb and finger the stopper is turned slowly, so every part of the surface is washed. If the rubber tube should become twisted it can

be prevented from turning with the other hand, providing the tube does not fit too tight. By careful washing not more than 250 cc. water will be required, which was determined by introducing 2 cc. strong hydrochloric acid and 40 cc. water, and washing until the acid disappears from the wash-water. The rubber tube *g* is secured by the pinch-cock, and the end is removed from the tube *b*. The bent tube *e* is drawn up so its end comes within 3 cm. of the stopper, and the long tip of the burette is carefully pushed further into the flask, and the barium hydrate is titurated by letting 20.5 cc. of the oxalic acid solution run in from the burette at once, and after gently shaking, one or two drops are added, and so on until the red color disappears. The data of one estimation are here given.

50 cc. of the barium hydr. = 24.5 cc. of the oxalic acid sol. Temperature 4° C. Barometric pressure 743.5 mm.

Capacity of apparatus, ...	6177 cc.
Deduct 50 cc. volumes Ba solution, . .	50
	6127 cc.

This volume, when subjected to normal pressure, would be $= \frac{6127 \cdot 743.5}{760} = 5993.9$ cc., and when reduced from 4° C. to zero would be $= \frac{273 \cdot 5993.9}{277} = 5907.3$ cc. It required 21.1 cc. oxalic acid solution, hence 3.4 milligrams CO_2 (the equivalent of 3.4 cc. oxalic acid solution) found in 5907.3 cc. air at zero and 760 mm. pressure, 1 milligram CO_2 at zero and normal pressure measures 0.5084 cc., hence $3.4 \times 0.5084 = 1.72869$ cc. CO_2 found. To find the number of volumes of CO_2 in 10,000 volumes air we have the following equation:

$$5907.3 : 1.72869 :: 10{,}000 : x$$

$$x = \frac{1.72869}{5907.3} = 2.926 \text{ volumes in } 10{,}000 \text{ volumes air.}$$

Estimations of carbonic acid in the air have been made in this laboratory several weeks under my direction, by Mr. B. F. Adams, who found that the principal source of error is the difficulty of ascertaining the correct temperature. If the apparatus is placed where it is thinly shaded the temperature will vary ten or fifteen degrees C. in 30 minutes, according as the rays of the sun pass through the apparatus or as reflecting bodies are warmed.

Even the temperature varies in different parts of the apparatus. When estimations are made, the temperature being below the freezing-point, and the barium solution is run into the apparatus, which necessarily has a temperature above the freezing-point, the air in the apparatus is warmed unequally. The difficulty is not removed by waiting until the fluid freezes, for during this time some air free of CO_2 may pass out of the apparatus by diffusion, and a false result be reached. With this apparatus, exercising the greatest care in determining the temperature and the atmospheric pressure, we have found that the quantity of CO_2 in the air is subject to slight variation at different times, but at present the number of estimations made is not sufficient to establish the maximum and minimum quantities during night and day, and during different seasons.

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ON THE SO-CALLED SILVER SUB-CHLORIDE.

BY SPENCER B. NEWBURY.

A year ago I published a series of experiments[1] on the action of solvents on silver chloride which had been blackened by exposure to light, from which the conclusion was drawn that in the blackening action of light no silver sub-chloride, but only metallic silver is formed. This was shown to be the case by the fact that if blackened silver chloride be treated repeatedly with a concentrated solution of sodium chloride, the silver chloride which has escaped reduction is completely dissolved, and pure, finely divided metallic silver remains.

The existence of silver sub-chloride has generally been assumed by chemists and writers on photography, and the formula Ag_2Cl has been supposed to represent its composition. A very complete outline of the literature of the subject is given by Von Bibra,[2] and need not be repeated here. There may be said to be three methods by which the so-called silver sub-chloride has been prepared, as follows:

[1] This Journal **6**, No. 6.

[2] Journ. fü prac. Chem., 1875.

1. Cavillier,[1] by passing excess of chlorine into an ammoniacal solution of silver chloride.

2. Wetzlar,[2] by action of iron or copper chloride on metallic silver.

3. Wöhler,[3] by the action of hydrochloric acid on silver sub-oxide or its salts.

In the last case Wöhler prepared silver sub-citrate by heating silver citrate to 100° in a current of hydrogen; he expressly states, however, that the existence of this substance is not proved, since a mixture of metallic silver with undecomposed citrate would behave in a similar manner. By treatment of the sub-chloride with potash and hydrochloric acid respectively, Wöhler obtained the corresponding silver sub-oxide and sub-chloride. No attempts seem to have been made to free these substances from possible admixtures of metallic silver or from unchanged citrate or chloride, in order to render the analysis of them conclusive. Von Bibra[4] prepared the so-called sub-chloride by the three methods given above, and concluded that No. 1 gives true sub-chloride; No. 2, a mixture of silver and silver chloride; No. 3, also true sub-chloride. In the last case Von Bibra assumed the reaction to be complete when the weight of the silver citrate, after heating six to seven hours in a current of hydrogen, remained constant; washed the product with water to remove free citric acid, treated with HCl, assumed the product to be pure silver sub-chloride, and established its formula to be Ag_4Cl_2.

In the hope of preparing the sub-chloride in a pure state by the action of some solvent which should remove possible impurities, I was led to make the following experiments:

1. The method of Cavillier, by action of chlorine on ammoniacal silver solutions, was tested. A stream of dry chlorine was conducted into a solution of silver chloride in ammonia. A slight gray precipitate was gradually formed, which, if the solution was kept strongly ammoniacal, consisted of finely divided silver wholly soluble in nitric acid. If, however, the ammoniacal solution was allowed to become nearly saturated with chlorine, mixtures of silver chloride and metallic silver, in varying proportions, were deposited, which on treatment with NaCl left a residue of gray metallic silver. From this I conclude that no sub-chloride is formed by this reaction. This is not remarkable, since all authorities agree that

[1] Journ. d. Pharm., 1830. [2] Jahresber., 1848. [3] Ann. Chem. Pharm. **30.** [4] *Loc. cit.*

the hypothetical sub-chloride is decomposed by ammonia, silver chloride being dissolved, and metallic silver remaining. The formation of the sub-chloride in a strongly ammoniacal solution was, therefore, not to be expected. The precipitation of a small quantity of metallic silver is perhaps owing to impurities in the chlorine which exercise a reducing action.

2. Finely divided silver was treated with a cold twenty per cent. solution of cupric chloride. Cuprous chloride was at once formed, but redissolved on addition of large excess of cupric chloride solution, leaving only white silver chloride.

If a few drops of stannous chloride solution are added to a solution of silver nitrate, a precipitate is formed which is at first white, but becomes black on stirring. Analysis of this precipitate showed silver and chlorine in varying proportions. If, however, stannous chloride be added in excess, a white precipitate consisting of silver chloride and a tin compound, probably oxychloride, is formed. If, therefore, dilute silver nitrate solution be gradually added to dilute stannous chloride solution until a dark precipitate begins to form, the precipitate then filtered off, and a further addition of silver nitrate made to the filtrate, a black precipitate is obtained. This was found to be metallic silver. It is evident that it is the stannous nitrate formed in this reaction which reduces the silver after all the chlorine has been precipitated, and also that no silver sub-chloride is formed.

3. I have made a large number of careful experiments on the preparation of silver sub-citrate by heating silver citrate to 100° in a current of hydrogen, following exactly the instructions of Wöhler and Von Bibra. The hydrogen was passed through a red-hot tube, and dried with sulphuric acid and calcium chloride. The silver citrate was very carefully dried in vacuum. Nevertheless, I did not find it impossible to obtain a constant weight as described by Von Bibra, nor to obtain a product of definite composition. Water was always given off, and a gradual decrease in weight took place, more or less rapid according to the rapidity of the stream of hydrogen. The silver citrate was changed to a black powder, under the action of a moderate current of gas, in about two hours, and was then found to have lost about two per cent. of its weight. If the action was continued several hours longer, the mass appeared to be partly fused, had a metallic lustre, and was found in some cases to have lost weight to the

amount of six per cent. On treating the product with water a solution resulted which was red by transmitted light, but invariably gray and cloudy by reflected light. It seems to me highly probable that this red color is caused by finely divided metallic silver. Hydrochloric acid produces in the solution a reddish precipitate, which on analysis was found to consist of silver chloride, with a minute amount of free silver. This shows that even when the action of the hydrogen is continued for several hours there is still a large amount of unchanged citrate present. I have made many attempts to separate the constituents of this black substance by solution in water, but obtained no results, because the red solutions are not clear, and give only silver chloride and traces of silver on treatment with HCl. It is evident that the statement generally contained in the text-books, that the argentous citrate dissolves in water with a red color, is incorrect.

On treating the black powder directly with hydrochloric acid, curdy brown precipitates were obtained, which contained varying proportions of silver and silver chloride, according to the duration of the action of the hydrogen. The substances were analysed by dissolving out the silver chloride by ammonia, and weighing residue of metallic silver. The formula Ag_4Cl_3 requires AgCl 81.8 per cent., Ag 18.2 per cent.; Ag_2Cl requires AgCl 57.1 per cent., Ag 42.9 per cent. Varying proportions of silver were found, according to the length of time treated. In some cases the amount of silver was found to exceed 60 per cent.

The substances obtained by acting upon the reduced citrate with hydrochloric acid were treated with cold solution of sodium chloride. In every case silver chloride was dissolved, and a residue of metallic silver was left. Wöhler, in the article referred to above, states that ammonium chloride solution produces this result. It is therefore evident that if the sub-chloride exists, it is of so unstable a character as to be readily decomposed by the ordinary solvents of silver chloride. There is, in fact, no evidence whatever of the existence of such a compound, or that the substances which have been supposed to be silver sub-chloride are anything but simple mixtures of silver and silver chloride.

In the case of the sub-citrate and sub-oxide the fact that Wöhler and Von Bibra obtained a product of constant weight on heating silver citrate in hydrogen has been assumed to be a proof of the existence of these substances. However, the hypothesis of the

formation of silver sub-citrate does not account for the *loss* of weight which has been in every case observed. The replacement of silver by hydrogen, and setting free of citric acid, calls for a gain in weight.

In my own experiments, which have been very numerous, and performed under a variety of conditions, an absolutely constant weight was in no case obtained. Both water and carbon dioxide were given off, in approximately equal quantities, as long as the action of the hydrogen was continued. On exhausting the products with ether a brown, tar-like mass was obtained, which contained free citric acid in considerable quantity, together with other substances which were not identified.

In conclusion, the loss of weight on heating silver citrate in a current of hydrogen, the formation of carbon dioxide, and residue of metallic silver left on treating the products with sodium chloride solution, seem to me to indicate that the reaction in question consists in the separation of silver and decomposition of citric acid, rather than in the formation of silver sub-citrate.

LABORATORY OF CORNELL UNIVERSITY, *March*, 1886.

Contributions from the Chemical Laboratory, U. S. Department of Agriculture.

VII.—KUMYS.

COMMUNICATED BY H. W. WILEY.

Fermented mare's milk has long been a favorite beverage in the East, where it is known as "Kumys." Although the Tartars and other Asiatic tribes use mare's milk for the manufacture of kumys, yet it is not the only kind that can be employed. Since the consumption of milk wine has extended westward, cow's milk is chiefly employed for making it, both in Europe and America. Mare's milk is considered most suitable for fermentation, because of the large percentage of milk sugar which it contains.

Koenig[1] gives as the average percentage of milk sugar in mare's milk 5.31. The same author[2] gives as a mean of 377 analyses of

[1] Nahrungsmittel, 46. [2] *Op. cit.* 40.

cow's milk 4.81 per cent. of lactose. Dr. Stahlberg,[1] who brought forty mares from the steppes of Russia to Vienna for the purpose of using their milk for kumys, found its percentage of lactose to be 7.26. On the other hand, ordinary mares that were kept at work gave a milk containing only 5.95 per cent. sugar.

The quantity of milk sugar in mare's milk is great, but there is a deficiency of fat and other solids. It appears to contain fully 89 per cent. water, while cow's milk does not have more than 87 per cent.

The process of manufacture is not uniform. In the Orient the mare's milk is placed in leathern vessels; to it is added a portion of the previous brewing, and also a little yeast. In 30 to 48 hours the process is complete. During this time the vessels are frequently shaken.

In the samples analysed by me the milk was treated with a lactic ferment and yeast. After 24 to 48 hours' fermentation the kumys was bottled. The bottles were kept in a cool place, not above 50° F., and in a horizontal position. When shipped to me they were packed in ice. After they were received in the laboratory they were kept on ice until analysed.

Method of Analysis.

Carbon Dioxide.—The estimation of the carbon dioxide was a problem of considerable difficulty. It was evidently impracticable to attempt opening the bottle and determining the gas in a portion of the contents. Fortunately I had access to a large balance which would turn with a milligram. On this I weighed the whole bottle, into the cork of which I had inserted a stop-cock such as used sometimes with a champagne bottle. With the bottle of kumys were also weighed two drying flasks containing concentrated sulphuric acid with their connections. Having obtained the weight of the whole, the gas was allowed to escape slowly from the stop-cock and to bubble through the sulphuric acid in the washing bottles. These, previously to being weighed, were filled with the gas from an ordinary carbonic dioxide generator. After the gas had almost ceased to flow the bottle of kumys was frequently shaken. It was also placed in a pail of water having a temperature of 30° C. After half an hour the gas ceased to come over. The whole apparatus was again weighed. The loss of

[1] Tymowski's Bedeutung des Kumys, 12.

weight gave the quantity of free carbon dioxide in the sample. After the analysis was completed the volume of the bottle was measured. It is fair to assume that at 30° the kumys still contained an equal volume of dissolved CO_2. In determining the total CO_2 this volume, or its equivalent weight, was added to that obtained by direct determination. By this method the CO_2 dissolved under pressure in the bottles is estimated separately from that which the kumys contains in solution under the weight of one atmosphere. Since it is of no importance to separate the gas into these two portions, I have given it altogether in the tables—in volume—by weight and in percentage by weight.

Acidity.—The samples examined showed under the microscope the acetic ferment, and a small portion of the acidity was therefore possibly due to acetic acid. It is the custom in giving the results of analyses of kumys to represent the whole of the acidity as due to lactic acid. The direct titration of the lactic acid in the kumys was attended with such difficulty that the attempt was abandoned. Whatever indicator was employed the change in color was so obscured that no sharp reaction could be obtained. To obviate this trouble the kumys was mixed with an equal volume of saturated solution of magnesium sulphate. After shaking the mixture it was poured through a linen filter. The first portions running through were turbid. After returning these to the filter it was quite clear. Better results were obtained by using with the kumys equal volumes of alcohol. The filtrate from this mixture was uniformly bright. In this filtrate the acid was estimated by titration with a standard sodic hydrate solution, making the proper corrections for dilution and using phenolphthalein as indicator. I would recommend this alcoholic method of clarification to all who may have occasion to determine acid in milk.

Alcohol.—The alcohol was estimated by distilling 500 cc. kumys with 10 cc. water until the distillate amounted to 500 cc. This being still turbid was redistilled with a small quantity of water. The final distillate of 500 cc. was used for the estimation of the alcohol in the usual way—viz.: by taking its specific gravity and calculating the alcohol from tables.

Milk Sugar.—The milk sugar was estimated by the method I recommended in a paper read at the Philadelphia meeting of the American Association for the Advancement of Science.[1]

[1] This Journal **6**, No. 5.

Fat.—Twenty grams of the kumys were evaporated to dryness in a Schaelchen, the whole rubbed to a fine powder and extracted with ether in a continuous extractor. The process of extraction lasted six hours. These results do not give accurate data for fat, since no allowance was made for the solubility of the lactic acid.

Albuminoids.—The albuminoids were estimated by evaporating five grams of the material in a Schaelchen, rubbing to a fine powder with soda-lime, and burning with the same in the usual way.

Water.—In a flat platinum dish partly filled with washed and dried sand, two grams of material were weighed and dried to a constant weight at 100°. The following are the results of the analyses:

No. of Sample.	Weight of Kumys in Grams.	Volume of CO_2 in Litres.	Weight of CO_2 in Grams.	Per cent. of CO_2 by Weight.	Per cent. of Acidity as Lactic Acid.	Per cent. of Alcohol.	Per cent. of Nitrogen.	Per cent. of Albuminoids.	Per cent. of Fat.	Per cent. of Water.	Per cent. of Milk Sugar.
1	747.415	2.543	5.009	.67	...	.87	.431	2.69	2.21	88.81	4.33
2	729.376	3.140	6.186	.85	.47	.66	.412	2.58	2.15	89.53	4.31
3	768.575	3.179	6.269	.82	.51	.69	.483	3.02	2.07	89.15	4.33
4	736.035	3.281	6.463	.88	.45	.81	.482	3.01	1.99	89.31	4.43
5	746.187	3.579	6.850	.91	.48	.86	.423	2.64	1.67	89.97	4.43
6	750.247	2.973	5.757	.77	.43	.70	.450	2.81	1.75	89.87	4.33
7	738.840	3.204	6.313	.85	.49	.73	.462	2.89	2.44	89.01	4.48
8	752.550	3.263	6.428	.85	...	.77	.450	2.81	2.34	88.87	...
Mean..	.....	.....	.....	.83	.47	.76	.449	2.56	2.08	89.32	4.38

It will be of interest to compare these results with those obtained by other analyses, both with kumys from mare's milk and from other sources. As a mean of fourteen analyses of mare's-milk kumys Koenig[1] gives the following figures—viz.: Water, 92.47 per cent.; alcohol, 1.84 per cent.; lactic acid, .91 per cent.; lactose, 1.24 per cent.; albuminoids, 1.97 per cent.; fat, 1.26 per cent.; ash, .31 per cent.; carbonic acid, .95 per cent.

The mean of two samples of kumys made of cow's milk is given by the same author as follows: Alcohol, 2.64 per cent.; lactic acid, 0.80 per cent.; milk sugar, 3.10 per cent.; albuminoids, 2.02 per cent.; ash, 0.45 per cent.; carbonic acid, 1.03 per cent.

In nine analyses of kumys[2] probably made of cow's milk the

[1] Koenig, Nahrungsmittel, 67-68. [2] *Op. cit.* 68.

means are as follows: Alcohol, 1.38 per cent.; lactic acid, 0.82 per cent.; sugar, 3.95 per cent.; albuminoids, 2.89 per cent.; fat, 0.88 per cent.; ash, 0.53 per cent.; carbonic dioxide, 0.77 per cent.

Interesting analyses of kumys prepared from mare's milk have also been made by Dr. P. Vieth.[1] The mares from which the milk was taken were on exhibition at the London International Exposition for 1884. These animals were obtained from the steppes of Southeastern Russia. The mares were from five to six years old and were cared for and milked by natives of the country from which they were taken. When milked five times daily the best of these mares gave from four to five litres of milk. It is to be regretted that the milk sugar, the most important ingredient of milk in respect of kumys manufacture, was estimated by difference. Eleven analyses of the mixed milk gave the following numbers:

Table of Analyses.

	Minimum.	Maximum.	Mean.
Sp. Gr.,	1.0335	1.0360	1.0349
Water,	89.74 per cent.	90.41 per cent.	90.06 per cent.
Fat,	0.87	1.25	1.09
Albuminoids,	1.71	2.11	1.89
Milk Sugar,	6.30	6.82	6.65
Ash,	0.26	0.36	0.31

The kumys made from the above milk had the following composition:

Sample No.	1.	2.	3.	4.	5.
Water.....	90.99 per ct.	91.95 per ct.	91.79 per ct.	91.87 per ct.	92.38 per ct.
Alcohol	2.47	2.70	2.84	3.29	3.26
Fat	1.68	1.13	1.27	1.17	1.14
Albuminoids	2.25	2.00	1.97	1.99	1.76
Lactic Acid..	0.64	1.16	1.26	0.96	1.03
Milk Sugar...	2.21	0.69	0.51	0.39	0.09
Ash.....	0.36	0.37	0.36	0.33	0.34

[1] Landw. Versuch. Stationen **31**, 353 *et seq.*

Sample No.	6.	7.	8.	9.	Mean.
Water.....	92.42 per ct.	91.42 per ct.	92.04 per ct.	91.99 per ct.	91.87 per ct.
Alcohol	3.29	2.25	2.84	2.81	2.86
Fat	1.20	1.22	1.10	1.44	1.19
Albuminoids	1.87	1.75	1.89	1.69	1.91
Lactic Acid..	1.00	0.70	1.06	1.54	1.04
Milk Sugar...	0.00	2.30	0.73	0.19	0.79
Ash.....	0.35	0.36	0.34	0.34	0.35

Collecting the above means together, we have the following

Comparative Table.

No.	Alcohol.	Lactic Acid.	Sugar.	Albuminoids.	Fat.	CO_2.	Water.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.	1.84	0.91	1.24	1.97	1.26	0.95	92.47[1]
2.	2.64	0.80	3.10	2.02	0.85	1.03	88.72
3.	1.38	0.82	3.95	2.89	0.88	0.77	89.55[1]
4.	2.86	1.04	0.79	1.91	1.19	.....	91.87
5.	0.76	0.47	4.38	2.56	2.08	0.83	89.32

Notes on the Above Table.

1. Mean of 14 analyses of kumys from mare's milk.

2. Mean of 2 analyses of kumys from cow's milk.

3. Mean of 9 analyses of kumys, origin unknown, probably from skimmed cow's milk.

4. Mean of 9 analyses of kumys made from mare's milk, London Exposition of 1884.

5. Mean of 8 analyses of kumys from cow's milk, made by Division of Chemistry, U. S. Department of Agriculture.

The comparison of the above results shows that the American kumys differs from that of other countries in the following points —viz.:

(*a*) The percentage of alcohol is quite low, and as a consequence the percentage of sugar is high.

(*b*) American kumys contains more fat, showing that it has been made from milk from which the cream had not been so carefully removed as in those milks from which the European kumys was made. But this statement is subject to the modification before mentioned in respect of the estimation of fat.

[1] By difference.

Mare's milk, as will be seen by the above analyses, contains much less fat than that of the cow and more sugar, thus making it more suitable for the production of kumys. Good cow's milk, however, is suitable for the manufacture of kumys after most of the cream has been removed. Should it be desired to make a kumys richer in alcohol, some milk sugar could be added. The samples of kumys analysed were all "young," as will be seen by the notes to follow.

The samples analysed were kindly furnished me by Mr. Julius Haag, of Indianapolis. This kumys makes a delightfully refreshing drink. When drawn from the bottle and poured a few times from glass to glass it becomes thick like whipped cream, and is then most palatable. It is much relished as a beverage, and is highly recommended in cases of imperfect nutrition by physicians. Those desiring to study the therapeutic action of kumys should consult the monographs of Biel,[1] Stahlberg,[2] Landowski[3] and Tymowski.[4]

Notes on Samples of Kumys analysed by Division of Chemistry.

No. 1. Bottled March 24; analysed April 8.
No. 2. Bottled March 25; analysed April 7.
No. 3. Bottled March 25; analysed April 7.
No. 4. Bottled March 24; analysed April 8.
No. 5. Bottled March 27; analysed April 7.
No. 6. Bottled March 28; analysed April 8.
No. 7. Bottled April 1; analysed April 8.
No. 8. Bottled April 1; analysed April 9.

ELECTROLYTIC ESTIMATIONS AND SEPARATIONS.

By Edgar F. Smith and E. B. Knerr.

In Vol. 5 of this Journal, Thomas and Smith described several methods by which they determined bismuth by electrolysis. We

[1] Untersuchungen ueber den Kumys und den Stoffwechsel waehrend der Kumyscur.
[2] Kumys, seine physiologische und therapeutische Wirkung. St. Petersburg.
[3] Du Kumys et de son rôle therapeutique.
[4] Zur physiologischen und therapeutischen Bedeutung des Kumys. Muenchen.

have continued this work, and find that from a sulphate solution containing free sulphuric acid the metal can be completely and rapidly deposited by the current.

Experiment 1.—The volume of liquid was 25 cc., in which were present .0081 gram metallic bismuth and 1 cc. H_2SO_4. Obtained .0081 gram Bi. We employed an electric current, generating 4 cc. oxy-hydrogen gas per minute. The time required for the precipitation was half an hour.

Exp. 2.—Volume of liquid 25 cc. Quantity of bismuth .0081 gram and 1 cc. H_2SO_4. Found .0081 gram Bi. The current produced 4.6 cc. oxy-hydrogen per minute. Half an hour was required for the precipitation.

Exp. 3.—Volume of liquid as in 2. Quantity of bismuth .0041 gram; H_2SO_4 1 cc. The current yielded 1.8 cc. oxy-hydrogen gas per minute. Time, forty-five minutes.

Exp. 4.—Volume of liquid 25 cc. Quantity of bismuth .0229 gram; 1 cc. H_2SO_4. Found .0228 gram Bi. Strength of current 1 cc. oxy-hydrogen gas per minute. Time, two hours.

Exp. 5.—Same as 4, but obtained .0229 gram Bi. Time, one and one-half hours.

These precipitations were made in the cold. The deposited metal was washed with water and alcohol, and then carefully dried in an air-bath.

We were led to try the separation of bismuth from iron under the above conditions. The following results indicate that this is possible in the presence of free sulphuric acid:

No. of Experiment.	Metallic Bi Present.	Metallic Fe Present.	Volume of Solution.	No. of cc. of H_2SO_4.	Bi Found.	Current Strength in cc. O. H. Gas per min.	Time Required for Precipitation.
1	.0041 gram.	.0059 gram.	30 cc.	1	.0040 gram.	.8	1 hour.
2	"	"	30	1	.0041	1.2	35 min.
3	"	"	30	1	.0041	1.2	1 hour.
4	.0082 gram.	"	35	1	.0082	.8	1¼ hrs.
5	"	"	40	2	.0082	1.4	2 hrs.
6	"	"	40	2	.0082	1.4	3½ hrs.
7	"	"	40	2	.0082	1.4	2 hrs.
8	.0041 gram.	"	30	2	.0040	1.2	2 hrs.

The iron was present as ferrous sulphate. In the following tests it existed as ferric-ammonium sulphate.

9	.0041 gram.	.0230 gram.	30 cc.	2 cc.	.0041 gram.	2.5	1 hour.
10	"	"	30	2	.0041	2.5	1 hour.
11	"	"	40	2	.0041	1.2	1 hour.
12	.1145 gram.	.0230 gram.	150	3	.1129	3	3 hrs.
13	.1542	"	150	3	.1538	3	3 hrs.
14	.1285	"	150	3	.1285	3	3 hrs.
15	.1285	"	150	3	.1281	3	3 hrs.

Bismuth can also be separated from nickel and cobalt under similar conditions. Our record of results shows the following:

No. of Experiment.	Metallic Bi Present.	Metallic Cobalt Present.	Metallic Nickel Present.	Volume of Solution.	No. of Free cc. H_2SO_4.	Metallic Bi Found.	Current Strength in cc. of O_2+H_2 gas per Minute.	Time Allowed for Precipitation.
	Gram.	Gram.	Gram.			Gram.		
1	.0041	.0104	.....	20 cc.	2	.0041	3.5	40 minutes.
2	"	"	.....	20	2	.0041	3.5	30 "
3	"	"	.....	25	3	.0041	3.5	2 hours.
4	.0229	.....	.0219	25	3	.0229	1	2 "
5	.0229	.0104	.....	25	2	.0231	1.4	2 "
6	"	.....	.0219	30	2	.0229	1	2 "

In all these experiments the filtrates from the deposited metal were examined for bismuth, and the precipitated metal for the others which were present in the solution with it. Although in Experiment 5 the amount of the bismuth is slightly in excess, no cobalt was discovered with it.

Manganese can also be included in the list of metals from which bismuth may be separated by electrolysis.

No. of Experiment.	Metallic Bi Present.	Metallic Mn Present.	Volume of Solution.	No. of cc. of Free H_2SO_4.	Grams Bi Found.	Strength of Current in cc. O_2+H_2 Gas per Minute.	Time Required for Precipitation.
1	.0229 gram.	.0236 gram.	50 cc.	2	.0229 gram.	3	2 hours.
2	.0229	.0236	20	2	.0229	1	2 "
3	.0229	.0236	20	2	.0229	1	1½ "

The deep purple color of permanganic acid appeared at the positive pole and was imparted to the entire solution.

Experiments were tried with solutions containing bismuth and zinc, bismuth and cadmium, bismuth and uranium, and several in which three or four metals, finally, also, one in which nine metals, were present with a definite amount of bismuth.

No. of Experiment.	Metallic Bi Present.	Al_2O_3 Present.	Cr_2O_3 Present.	Metallic Fe.	Metallic Co.	Metallic Ni.	Metallic Cd.	Metallic Mn.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
1	.0229	.....	.....	.....	.....	.....	.....	.....
2	"	.....	.....	.....	.....	.....	.....	.....
3	"	.....	.....	.....	.....	.....	.....	.....
4	"	.....	.....	.....	.....	.....	.6057	.....
5	"	.....	.....	.....	.....	.....	.....	.....
6	"	.....	.....	.....	.....	.....	.....	.....
7	"	.....	.....	.....	.....	.....	.....	.....
8	"	.0124	.0063	.....	.0104	.0219	.....	.....
9	"	.0124	.0126	.0230	.0140	.0219	.....	.....
10	.0229	.0124	.0126	.0230	.0140	.0219	.0057	.0236

No. of Experiment.	Metallic Ur.	Metallic Zn.	Volume of Solution.	Free cc. H_2SO_4.	Bi Found.	Strength of Current in cc. O. H. Gas per Minute.	Time.
	Gram.	Gram.			Gram.		
1	.....	.0393	20 cc.	2	.0223	1	2 hours.
2	.....	"	20	2	.0224	1	3 "
3	.....	.....	50	2	.0227	1.1	1¾ "
4	.....	.....	50	2	.0229	1.1	1⅓ "
5	.0099	.....	20	1	.0229	2	¾ "
6	"	.....	20	1	.0225	2	35 minutes.
7	"	.....	20	1	.0229	2	50 "
8	.....	.0393	100	3	.0229	1.4	2 hours.
9	.....	.0393	100	5	.0229	3	2 "
10	.0099	.0393	150	3	.0229	1.2	4 "

In the *Berichte der deutschen chemischen Gesellschaft* **19**, 325, attention has been called to the fact that mercury in a nitric acid solution can be determined with great accuracy in the electrolytic way. More than a year ago Mr. W. S. Hoskinson, of this laboratory, obtained the following results, using a mercurous nitrate solution:

	Hg required.	Hg obtained.
1	.0141 gram.	.0139 gram.
2	...	.0138
3	...	.0139
4	...	.0139
5	...	.0139

As the strength of the electric current employed in these determinations was not considered, we took occasion to ascertain this

fact by additional experiments with similar solutions. Our record shows the following data:

No. of Experiment.	Hg Present.	Hg Found.	Volume of Solution.	Cc. of Free HNO_3.	Strength of Current in cc. of O.-H. Gas per Minute.	Time.
1	.0911 gram.	.0908 gram.	25 cc.	1	4.3	30 minutes.
2	"	.0911	25	½	4	30 "
3	"	"	25	"	4	45 "
4	"	"	25	"	4	45 "
5	"	"	30	"	4	45 "
6	"	.0912	30	"	4	45 "

The mercury separated as a compact, shining deposit; it was washed with water and alcohol, and dried over sulphuric acid.

Yver[1] recommends an acetate solution containing free acetic acid when separating zinc and cadmium by the electric current. Eliasberg[2] has since directed attention to the necessary current-strength in order that the method may be rendered more successful. We have employed this method in about thirty separations of these two metals, and would emphasise the fact that the current should be carefully regulated. Some experience is requisite to insure satisfactory results. Our best results were obtained from a current generating not much more than .1 cc. oxy-hydrogen gas per minute. This is less than that given by Eliasberg. Our separations were made in crucibles of about 40 cc. capacity.

With the tartrates of zinc and cadmium we hoped to get better results. We first operated with a solution containing a definite quantity of cadmium, together with a slight excess of tartaric acid. The electric current employed produced 3.4 cc. oxy-hydrogen gas per minute. Heat was applied to the solution. .0060 gram metallic cadmium was deposited in about forty-five minutes. We subsequently electrolysed a solution of 40 cc. volume, containing .0060 gram Cd and .0185 gram Zn, together with 2 grams of sodium tartrate, and an excess of tartaric acid. After the current, generating .5 cc. oxy-hydrogen gas per minute, had acted for three hours, we obtained .0060 gram cadmium. The metal was not only fully precipitated, but was free of zinc.

[1] Bulletin **34**, 18. [2] Zeitschrift für anal. Chemie **24**, 548.

Additional experiments:

1. With the same quantities of cadmium and zinc as above we got .0057 gram Cd. Current = .4 cc. oxy-hydrogen gas per minute.

2. Same as 1. Current = .4 cc. oxy-hydrogen gas. Time, 2½ hours. Found .0054 gram Cd.

3. Same as 2. Time, 4 hours. Obtained .0060 gram Cd.

4. Same as 3. Current = .5 cc. oxy-hydrogen gas. Found .0060 gram Cd.

5. Volume of solution 60 cc., in which there were .0120 gram Cd and .0185 gram Zn, 2 grams sod. tartrate, and an excess of tartaric acid. Current = .5 cc. oxy-hydrogen gas per minute. Time, 4½ hours. Found .0115 gram Cd, free from zinc.

6. With same conditions as in 5, obtained .0116 gram Cd.

The deposition of metal was very rapid at first. The last traces are, however, difficult to remove.

WITTENBERG COLLEGE, SPRINGFIELD, O., *May* 6, 1886.

ON THE DETERMINATION OF ABSOLUTE NEUTRALITY.

BY J. R. DUGGAN.

As some confusion exists in the use of the terms "acidity" and "alkalinity," it seems necessary to state the exact sense in which they are used in this article. It is customary to consider alkalinity as having some connection with the property of certain bodies to combine with acids to form salts and water, but this is more properly called basicity, and it is by no means necessary that a base should be alkaline, or that an alkaline body should be a base. Sodium carbonate is distinctly alkaline, but does not combine with acids, while phenol, which even has acid properties, will, under proper conditions, unite with an acid to form a salt and water. With the term acidity the difficulty is greater, because there is no other word in common use that may be used to express one of its

meanings. There certainly are bodies, however, that show acid properties, but do not unite with bases to form salts, as many salts of the heavy metals; while other bodies that are neutral or slightly alkaline will unite with bases to form salts and water, as, for example, primary alcohols. In fact, a certain substance may act as an acid or base according to circumstances, but it cannot show both acidity and alkalinity. Unless otherwise stated, the term acidity when used in this article means the opposite of alkalinity, rather than of basicity. The necessity for this distinction will, I hope, be better appreciated when the following experiments are taken into account. It must not be understood from the above that the acidity of *acids* and the alkalinity of *bases* has no connection with the *avidity to combine* or *affinity* which acids show for bases and bases for acids.[1]

The Influence of Mono- and Polybasic Acids, in the Presence of their Sodium Salts, on the Conversion of Starch by Diastase.

These experiments were undertaken in order to compare the action of organic acids and alcohols on soluble ferments with their action on organised ferments, and are a continuation of some former studies on the relation between chemical constitution and physiological action.[2] One of the principal objects in the work was to ascertain whether or not the action of acids on diastase was proportional to their affinity. Diastase was selected because it is a typical soluble ferment, and one whose action in converting starch into dextrin and sugar is comparatively simple and easily measured. As some of the results obtained are of chemical interest, aside from any connection they may have with physiology, it seems best to consider these separately. As the subject is still under investigation, what is contained in this article must be taken to a certain extent as a preliminary notice.

The amount of acid necessary to retard the action of diastase has been investigated by several observers, and with widely different results in each case; but the recent work of Chittenden and Cummins[3] has shown that this is due for the most part to the fact that different specimens of malt-extract and starch contain varying amounts of proteid matter, which combines with the acid and

[1] See Muir's Principles of Chemistry, p. 401 *et seq.*

[2] This Journal **7**, 62.

[3] Studies Lab. Physiol. Chem. Yale College, 1884–5, p. 36.

prevents its retarding action. They find that the acid proteids which are thus formed may even accelerate the action of the ferment. I have found that the normal salts of many acids also prevent the retarding influence of acids, just as they retard or prevent the action of acids in inverting cane-sugar.[1] By preparing reagents as free as possible from foreign substances, and using very dilute starch-paste, I have been able to reduce the amount of even comparatively weak acids, such as formic, that is necessary to distinctly retard diastatic action, to 0.0002 per cent. (1 to 500,000), while 0.001 per cent. entirely prevented action. It is evident from this that the common statement that diastase acts best in a slightly acid solution applies only to such as contains proteids or salts with which the acid may combine, and not remain free to act on the diastase. If it were possible to prepare both starch and diastase perfectly pure, it is probable that any appreciable quantity of the stronger acids would prevent the action of the ferment.

The influence of alkalis on diastase is even more marked than that of acids; so it will be seen that it is an extremely delicate indicator of acid or alkaline reaction. The practice of using litmus, phenolphthalein, and similar substances, for this purpose is so common that we fall into the belief that they show absolute neutrality; but this is by no means true, and a disregard of this point must lead to grave errors in chemical and physiological investigations. A number of substances will react acid with one indicator and alkaline with another, as, for example, di-sodium phosphate;[2] or we may have an acid or base that is too weak to affect the indicator, as boric acid or urea, in which case the solution will appear neutral when it is not. We may also have a strong acid combined with such a base, or *vice versa*, so that the acid will act on the indicator as though it were uncombined, but it certainly does not act in many chemical reactions or on living organisms in such a manner. As an example, sodium borate or carbonate acts on some indicators as caustic soda, and can be titrated as such, but a more striking illustration is the titration by means of phenolphthalein of the acid combined with alkaloids as free acid.[3] While sodium borate and carbonate are alkaline, they are certainly not as much so as caustic soda, and the same is true of the acid in

[1] Jour. f. prak. Chem. **85**, 321, and (2) **32**, 32. [2] Compt. Rend. de l'Acad. **100**, 55.
[3] Jour. Pharm. (5) **11**, 495.

morphine sulphate and similar salts of the alkaloids. With nearly all indicators the presence of proteid matter does not affect the accuracy with which acids may be determined, but, as already mentioned, the work of Chittenden and Cummins has shown that there is present in such cases a compound which acts entirely differently from the free acid. By the selection of indicators to suit the conditions something may be done to avoid these difficulties, but there will still remain many cases of acidity or alkalinity which cannot be measured by any of the ordinary methods. Ostwald[1] has shown that each acid has a definite strength or affinity-constant which conditions the specific intensity of any action brought about by that acid. This constant may be determined by several methods, the most reliable, since it is free from secondary reactions, being based on the rate at which the acid inverts cane-sugar. It appears that each base also has its affinity-constant, although the methods by which this may be determined are not so well developed as in the case of acids. Let us now suppose that two salts are formed by the addition of two acids to a base, as sodium chloride and sodium acetate. These salts are neutral to all color indicators; and if this neutrality is absolute, it would seem that an equivalent of any acid can neutralise, and is neutralised by, an equivalent of any base without regard to its affinity, for these two acids differ greatly in this respect. This is the same as saying that the acid properties of an acid, and the alkaline properties of a base, are entirely destroyed when the two combine to form a normal salt. That such is not the case may be shown with the ordinary color indicators, but only when there is very great difference in the affinities of the base and acid, as with alkaline carbonates or sulphates of some of the heavy metals. That sodium chloride does not turn blue litmus red, and sodium acetate the reverse, is due to the fact that litmus is not sufficiently delicate as an indicator to respond to the comparatively weak acid and alkaline reactions of these salts. That the salts are respectively acid and alkaline is shown beyond doubt by the investigations of Löwenthal and Lenssen,[2] and more especially of Spohr,[3] on the inversion of cane-sugar, and by their influence on diastatic action in the presence of acids. The addition of sodium chloride to hydrochloric acid increases the rate at which it inverts cane-sugar, while sodium acetate has an opposite effect on acetic acid. The amount of hydrochloric acid required to retard to a

[1] Jour. f. prak. Chem. (2) **29**, 57. [2] *Ibid.* **85**, 321, 401. [3] *Ibid.* (2) **32**, 32.

certain extent (50 per cent.) the action of diastase is so small that it is difficult to say if this is diminished by the addition of sodium chloride; but the increase in the amount of acetic acid that is made necessary by the addition of sodium acetate is very marked, and is proportional to the amount of the salt added. This is very well shown by the following table. The amount of conversion with diastase and starch-paste alone is shown by the control experiment. The solutions were in each case made up to 100 cc., and the flasks containing them were kept in a water-bath at 55° C. for thirty minutes, when the action of the ferment was stopped by the addition of an excess of caustic soda. The amount of sugar formed was determined volumetrically by Fehling's solution, and calculated as maltose.[1]

TABLE I.

	NaOH.	$C_2H_4O_2$.	Maltose.	Per cent. of retardation.
1	.000 gram.	.000 gram.	.420 gram.	...
2	.000	.001	.204	51.4
3	.005	.045	.215	48.8
4	.010	.090	.213	49.3
5	.015	.135	.210	50.0
6	.020	.180	.210	50.0
7	.030	.270	.207	50.7
8	.040	.360	.205	51.2

It will be seen that the retardation is not quite constant, but increases slightly with the amount of alkali and acid present. This is probably due to the action of the substances aside from any condition of alkalinity or acidity. This secondary action, as it may for convenience be called, is very marked with some substances, such as salts of the heavy metals, and when such is the case, of course the reaction cannot be used to measure alkalinity or acidity; but with the alkali metals and most organic substances, the error from this source is very small unless they are used in large quantities. If the retarding action of any substance is partially or entirely prevented by the presence of an acid, it seems fair to conclude that it is to that extent due to alkalinity of the substance, and *vice versa;* but when it is not affected by either acids or alkalis, it is evident that it acts on the ferment in some other manner.

[1] For greater details of the method used in determining diastatic action, see this Journal 7, 306.

The table shows that in the presence of 5 mgrs. of caustic soda, 45 mgrs. of acetic acid are necessary to produce the amount of retardation caused by 1 mgr. acting on the starch and diastase alone. (Of course the use of reagents of greater or less purity will cause the amount of acid to vary, so that more or less than 1 mgr. may be required; and with perfectly pure materials, it is impossible to say to what extent this would be reduced.) Now 7.5 mgrs., or one-sixth of the 45 mgrs. of acid, combine with the 5 mgrs. of caustic soda to form normal sodium acetate; and we must suppose that this normal salt neutralises to a certain extent the remaining 37.5 mgrs., or five equivalents of acid. In order to do this sodium acetate must be an alkaline salt, or one in which the affinity of the acid is less than that of the base. The following table shows this to be the case:

TABLE II.

	NaOH.	$C_2H_4O_2$.		Maltose.	Per cent. of retardation.
1	...	...		0.428 gram.	...
2	0.020 gram.	0.015 gram =	½ equiv.	0.000	100
3	"	0.030	1 "	0.363	15.0
4	"	0.060	2 "	0.428	.00
5	"	0.090	3 "	0.396	7.5
6	"	0.120	4 "	0.360	15.9
7	"	0.150	5 "	0.290	32.2
8	"	0.180	6 "	0.225	47.4
9	"	0.210	7 "	0.152	64.5

The second experiment of this series is introduced to show that an excess of caustic soda acts as though there were no acetate present; that is, that the normal salt does not prevent the action of alkalis as it does that of acids. In this case one-half the soda combines with the acid, leaving 10 mgrs. free; but if such an amount of acid is used that only 1 mgr. is left free, the result would be the same, no action taking place. In the third experiment the acid and base were added in the proportion of their combined weights, so there was present only the normal salt. This retards the reaction 15 per cent.; but when another equivalent of acid is added, as in No. 4, the conversion is the same as in the control experiment, showing that the solution is neutral. When more than two equivalents of acid are added, we again get retardation from acidity.

If, now, formic acid is used instead of acetic, a similar series is obtained, except that the retardation from the normal salt is not so great, and the excess of acid required to prevent retardation is considerably less. With propionic acid the reverse is the case, the retardation from the normal salt being greater, and more than two equivalents of acid to one of base being necessary to prevent retardation. It is evident from this that in sodium formate the alkali is more nearly neutralised than in the acetate, while it is less so in the propionate. It will be seen from this that this reaction can be utilised to determine the power that different acids have for neutralising an alkali. Instead of determining the excess of acid which was necessary to neutralise the normal salt, it was found that more accurate results could be obtained, without affecting the proportion, by finding the amount required to retard the reaction ·50 per cent. As a standard for comparison a flask containing five equivalents of acetic to one of sodium acetate was used, instead of one containing only diastase and starch. This retarded about 50 per cent., but as it was desirable simply to compare the acids among themselves, the actual degree of retardation was of little importance. The amounts of various acids in excess of the one equivalent which combined with the caustic soda to form the normal salt, which were necessary to produce the same retardation as the five equivalents of acetic, are given in the first column of Table III. They are for convenience expressed in their caustic soda equivalents in the second column. The figures are the amounts required with 20 mgrs. of caustic soda, as this was the amount generally used, but in some of the series 40-mgrs. were used. The results are the mean of several series.

TABLE III.

Acid.	Required Amount.	NaOH Equivalent.
Formic,	14.4 milligrams.	12.5 milligrams.
Acetic,	150	100
Propionic,	246	133
Isobutyric,	273	124
Lactic,	27.0	12.0
Benzoic,	82.4	27.0
Phenylacetic,	129	38.0
Oxalic,	6.30	5.60
Succinic,	109	74.0
Pyrotartaric,	99.0	60.0

Malic,	38.5	23.0
Tartaric,	18.4	9.80
Fumaric,	18.3	12.6
Phthalic 1 : 2,	42.5	20.5
Citric,	46.4	29.0

These figures represent the amount of each acid necessary to produce a certain degree of acidity in a solution which contains the amount of salt formed by the combination of the acid with 20 mgrs. of caustic soda. Of course the affinity of each of the acids is less than that of caustic soda. If acids having a coefficient of affinity greater than that of the base were used, it would then become necessary to use a certain amount of some alkali to prevent the retardation caused by the normal salt, since it would be acid. This part of the subject has not yet been investigated, except to a very slight extent.

The neutralisation of an alkaline base by an acid of lower affinity may be divided into two stages—the saturation of the base to form a normal salt, and the neutralisation of the alkaline salt. The amount of acid necessary to accomplish the first of these depends, of course, upon its combining weight and the number of replaceable hydrogen atoms it contains. In order to determine if the amount required in the second stage depends upon the affinity of the acid, the following experiments were made. Since, according to Ostwald,[1] the power which an acid shows in inverting cane-sugar is the most reliable measure of its affinity, I determined the amount of each of the acids that is required to convert a given amount of cane-sugar under fixed conditions. 10 cc. of a 20 per cent. solution of cane-sugar was, in each case, made up to 50 cc. by the addition of the acid and water. The solutions were heated to 70° C. before mixing, and kept in a water-bath at this temperature for thirty minutes. The reaction was stopped by the addition of a slight excess of caustic soda, and the sugar determined by Fehling's solution as dextrose. The standard for comparison was in each series a flask containing the above amount of sugar and 0.150 gram of acetic acid. By using this as a control experiment, any slight variation in time or temperature caused no error, as all the flasks were under the same conditions. The first column in Table IV shows the amount of each acid required to produce the same amount of conversion as 0.150 gram of acetic. In the second

[1] *Loc. cit.*

column the acids are expressed in their soda equivalents, while the third is a repetition, for comparison, of the second column of Table III. The fourth column gives the percentage proportion between the figures in the second and third columns, those in the second being taken as 100.

TABLE IV.

Acid.	Inversion of Cane Sugar. Required amount.	NaOH equivalent.	NaOH equiv. of am't req'd to neutralise the normal salt.	Per cent. proportion.
Monobasic.				
Formic,	13.8 mgrs.	12.0 mgrs.	12.5 mgrs.	104
Acetic,	150	100	100	100
Propionic,	255	138	133	96.4
Isobutyric,	286	130	124	95.4
Lactic,	26.1	11.6	12.0	103
Benzoic,	85.0	27.9	27.0	96.4
Phenylacetic,	125	37.3	38.0	102
Dibasic.				
Oxalic,	3 71	3.30	5.60	169
Succinic,	66.4	45.0	74.0	164
Pyrotartaric,	57.8	35.0	60.0	171
Malic,	20.8	12.4	23.0	(185)
Tartaric,	10.9	5.80	9.80	169
Fumaric,	10.9	7.50	12.6	168
Phthalic 1 : 2,	11.6	5.60	20 5	366
Tribasic.				
Citric,	15.7	9.80	29.0	296

It is evident from this table that the amount of a monobasic acid required to neutralise an alkaline salt of that acid is proportional to its affinity as measured by its action on cane-sugar. Spohr has reached practically the same conclusion from his study of the influence of normal salts on the inversion of cane-sugar by acids.[1] In the case of dibasic acids the table shows that more is required to neutralise the salt than with monobasic acids, or that the normal salt is more alkaline than it would be if formed from a monobasic acid of the same affinity-constant. For example, it was found that normal sodium succinate retards the action of diastase more than an equivalent quantity of sodium acetate, although succinic acid inverts sugar more rapidly than acetic, and might therefore be supposed to form a less alkaline salt. It must be remembered that in

[1] Jour. f. prak. Chem. (2) **32**, 46.

comparing the action of acids, the carboxyl groups are compared, so that half an equivalent is used in the case of dibasic acids. To explain this greater alkalinity of salts of dibasic acids, we must suppose that each atom of sodium not only neutralises the carboxyl group into which it enters, but influences in some manner the other similar group in the molecule. There is reason to suppose that a molecule of oxalic acid inverts cane-sugar more rapidly than would two molecules of an acid having the formula COOH, or that the affinity of polybasic acids is increased by a mutual reaction between the carboxyl groups.[1] This being true, it follows that the neutralisation of one carboxyl group in such an acid must diminish the affinity of the remaining ones. In the case of phthalic acid this action is much more marked than with acids of the paraffin series. This cannot be due to experimental error, as this acid was examined very carefully; but it will be necessary to examine other acids in which we have what is termed the ring structure before attempting any explanation of this. In the case of the one tribasic acid examined, the amount of acid required to neutralise the salt is, as would be supposed, more than with either mono- or dibasic. As all of these results were obtained from the use of a monacid base, it does not follow that they would hold good for a polyacid base.

This greater alkalinity of salts of polybasic acids is very well shown in the case of phosphoric acid, for although a molecule of this acid converts sugar more rapidly than three molecules of acetic, it is with considerable difficulty that the acid can be made to form a normal sodium salt. In other words, the acidity of the acid is so well neutralised by one or two atoms of sodium that it is only with difficulty that it can hold a third. The reverse of this tendency of the weaker polybasic acids to form only primary or secondary salts is seen in the frequent formation of basic salts when a strong acid combines with a slightly alkaline base.

The Influence of Alcohols on Diastatic Action.

In the presence of about 7 per cent. by weight of ethyl alcohol the action of diastase is retarded one-half, but if there is added to 100 cc. of the solution about 3 mgrs. of acetic acid, there is but little retardation. That the retardation by the alcohol which is prevented by this minute quantity of acid is due to its alkalinity is borne

[1] Muir's Principles of Chemistry, 470.

out by the fact that the inversion of cane-sugar by acids is also retarded by the presence of alcohol. Titration before and after the experiment showed that there was no etherification, as would be supposed, considering the extreme dilution of the acid. It seems natural to conclude from this that there is here a condition similar to a basic salt in which a great many molecules of the base are combined with one of acid, for if such is not the case, it is difficult to explain the action of the acid in neutralising the alcohol. Under these conditions the alcohol shows alkaline, but not basic properties, since it does not unite with the acid to form an ester (salt). This action of alcohols is of considerable physiological interest, and I hope by further study to throw some light on their action on the living organism. As we approach the acid-phenols through the secondary and tertiary alcohols we find that they act less and less on diastase, until phenol is reached, when we get decided action from its acidity. I hope to verify the results I have obtained by a further study of the influence of alcohols on the inversion of cane-sugar by acids, and until that is done, a lengthy discussion, including the different alcohols, would be premature.

As the value of any method depends to a great extent upon its accuracy, it will be well to notice the experimental errors that show themselves in the above determinations. An examination of the fourth column of Table IV shows that these may amount to several per cent. Of course, any impurity in the acid is likely to produce an error, and this is probably the cause of the rather large amount of malic acid required to neutralise the normal salt. In the experiments with diastase there is probably a small amount of the acid used up in combining with the proteid matter and salts which cannot be entirely removed from the starch and diastase solution. It will be seen that rather more of the acids which have a high affinity constant is required than the theory calls for. As they are used in small amounts, any proteid matter present would render inactive a proportionately larger quantity of these than of the weaker acids. Ostwald has shown that the results obtained from the inversion of cane-sugar depend to a slight extent on the concentration of the solutions used. When the errors from these and other causes happen to be all on the same side, it is not surprising that they should amount to several per cent. I think the results obtained, however, show that the method is valuable, and will assist in the important work that Ostwald has undertaken. It cannot be

doubted that the physiological action of organic acids is dependent to a great extent on their affinity, and the determination of affinity-constants will probably be of as much value to physiological as to pure chemistry.

In conclusion, I do not think it will be out of place to offer a protest against the custom of calling salts acid or neutral according to whether a part or all of the hydrogen is replaced. Primary or mono-sodium carbonate is not an acid salt, nor is the normal salt neutral. This is an extreme case, but it is taken to show that such a use of these terms is incorrect even if we use only the ordinary color indicators.

I am under many obligations to Prof. Remsen for suggestions and for advice which he has kindly given me during the progress of the work.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, *May*, 1886.

NOTE.

Etched Figures and Arrangement of Atoms.

The method of "etched figures," which within the past few years has proved so successful in the detection of hemihedral and tetartohedral forms on crystals which appear to be holohedral, bids fair to play some part in the discussion regarding the position of the atoms in the molecules of crystalline substances.

When Linnaeite (Co_3S_4) is treated with acids its cubic faces are most readily attacked. When treated with fused potash, however, the solution takes place most rapidly in the direction of the dodecahedral planes.

This fact leads F. Becke[1] to observe that probably the cobalt atoms in the molecule are turned towards the cubic faces and the sulphur atoms towards the dodecahedral faces.

Whether the use of this method will throw any light on the position of the atoms in space, is doubtful. It is probable, however, that it will help to an understanding of the forces which act in the formation of crystals. W. S. B.

[1] Tschermak's Min. und Petrogr. Mitt. **8**, 195.